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subject: Cook-off Experiments with Surrogate WIPP Drum Contents

Executive Summary

A number of cook-off experiments were performed to provide understanding of potential thermal ignition of drum 68660 in the February 14, 2014 radiation release at WIPP. Testing was begun according to the plan provided in Appendix B, and deviated significantly based on initial findings and other information developed during the testing. Two general types of experiments were performed: ones with nitric acid neutralized to varying degrees with Kolorsafe neutralizer, and ones with no added free liquid. Results indicate that reactivity is greater in the dry mixture, and that Fe nitrate and Ca nitrate play significant roles in ignition behavior whereas Pb nitrate, Cr nitrate, and oxalic acid do not. Within mixtures with liquid, very little exothermic behavior is observed with Swheat and water, but adding neutralized acid and nitrate salts results in significant reactivity and ignition. This behavior is suppressed by liquid water, and ignition occurs after the water has fully vaporized, although it is not clear if ignition occurs quickly because of the relatively high wall temperature at the end of the vaporization process.

Following are key observations and conclusions from these experiments:

1. Comparison with Los Alamos National Laboratory (LANL) results:
    a. Extrapolation of low temperature exothermic reactions over a range of heating rates suggests these may occur near ambient temperature, with Swheat, Mg nitrate, Na nitrate, Fe nitrate, and Ca nitrate.
    b. Ca nitrate and Fe nitrate both have strong effects on thermal runaway temperatures. Fe nitrate has a significant role in low temperature reactions.
    c. Pb, Cr, and oxalic acid have little effect on ignition of the dry mixtures.
2. Exhaust gases do not easily ignite.
3. Confinement matters. Reaction rates drop dramatically when temporary clogs release. Sealed tests have not been run (in general). Pressures involved are not known.
4. Vaporization of water has a strong effect on exothermic reactions in all mixtures.
5. Thermal properties have been estimated. Thermal properties vary primarily with presence of moisture. Addition of salts to Swheat has a lesser effect.
6. In most cases, materials are not entirely consumed during combustion. Solid residue with similar total volume is left behind.

7. Temperatures were as high as 400-600°C in thermal runaway with mixtures that include liquid. Measured temperatures are were as high as ~300°C in dry mixtures. Ignition in dry mixtures were more local with high temperature rates than in the wet mixtures.
8. Neutralized acid and Swheat is reactive than Swheat and water.
9. Adding Mg and Na nitrates to Swheat and neutralized acid increases reactivity, although this may be due to reduction in the amount of liquid present.
10. No mixtures studied to date react as violently as a conventional explosive or propellant.
11. Small-scale tests exhibit phenomena that may have occurred in drum 68660. Cook-off behavior may not be the same at larger scales.
12. Ignition events, including some of substantial violence, demonstrate that venting can be overcome by rapid gas generation, although the vent in these experiments was not scaled to the vent used on WIPP drums.

1. Test Summary

Table 1 lists the tests performed to date and details of the materials and other test conditions. Abbreviations used in Table 1 are listed below. Unless noted otherwise in Table 1:

1. Tests were vented.
2. Heating rate was 5°C/min.
3. Swheat was included.

Table 1 uses the following abbreviations:

- DI – Deionized
- NNA - Neutralized Nitric Acid: 3.3M Nitric Acid + Kolorsafe to pH 7, equal volumes
- ONNA – Over-neutraluzed Nitric Acid: 3.3M Nitric Acid + Kolorsafe to pH 7, equal volumes, plus 5.26 ml Kolorsafe per 100 ml final solution.
- UNNA - Under-neutralized Nitric Acid: 3.3M Nitric Acid + Kolorsafe to pH 7, equal volumes, plus 5.26 ml 3.3M nitric acid per 100 ml final solution.

Table 1. Summary of tests and test parameters. Sweat was used in all tests. Unless noted, all tests were vented, and heated at 5°C/min.

Test	Date	Liquid	Salts	Notes / Results
Exp386	10/20/14	Tap Water	None	Sealed
Exp387	10/27/14	DI Water	None	2°C/min to study low temperature reactions. Small exotherm.
Exp388	10/30/14	NNA	None	Two exotherms after water vaporized.
Exp389	11/4/14	DI Water	None	No exotherm until end of ramp.
Exp390	11/7/14	NNA	Na and Mg nitrates	One exotherm after water vaporized – temperatures to 600°C.
Exp391	11/11/14	UNNA	Na and Mg nitrates	Compatibility test with UNNA and Mg and Na nitrates.
Exp392	11/12/14	UNNA	Na and Mg nitrates	Compare under-neutralized acid to neutralized in Exp390.
Exp394	11/18/14	ONNA	Na and Mg nitrates	Too much salt used due to density measurement error. Strong effect on phase change. Violent – launched top insulation.
Exp395	11/20/14	ONNA	Na and Mg nitrates	Same as Exp394.
Exp396	11/24/14	ONNA	Na and Mg nitrates	Compare over-neutralized acid. Large exotherm and lots of gas.
Exp397	11/25/14	ONNA	LANL SA mix	Compatibility test with LANL Stream Analyzer mix and ONNA.
Exp398	11/26/14	ONNA	LANL SA mix	LANL salt estimate. Most TCs failed early. Slow build to ignition (not violent) and slow burn.
Exp399	12/3/14	ONNA	Na and Mg nitrates	Pulled vacuum to draw off water, but it didn't work.
Exp400	12/4/14	N/A	Remains of Exp397	Attempted to ignite, but did not work
Exp401	12/8/14	ONNA	LANL SA mix	Ramp and hold at 105°C. Water did not fully vaporize after 4 hours. No ignition. Re-heated to 105 C and held for >4 hours with no ignition.
Exp402	12/10/14	ONNA	LANL SA mix	Ramp and hold at 110°C. No ignition after about 5 hours.
Exp403	12/11/14	None	LANL WB-4 mix w/out 0.2% water	Exotherm or phase change starting around 66C.
Exp404	12/12/14	None	LANL WB-4 mix w/out water, Pb, or Cr	Exotherm started around 71°C.
Exp405	12/15/14	None	LANL WB-4 mix w/out water, Pb, or Cr	Open SITI. 2°C/min. No ignition up to 290°C. Material expanded significantly.
Exp406	12/16/14	None	LANL WB-4 mix w/out water, Pb, Cr, or oxalic acid	Attempted plume ignition, but test was very violent
Exp407	12/17/14	None	LANL WB-4 mix w/out water, Pb, Cr, Ca, or oxalic acid	No eutectic, still some exothermic activity at low temperature, but ignition at higher temperature.

Exp408	12/19/14	None	LANL WB-4 mix w/out water or Fe nitrate	Low temperature reactions are suppressed and ignition occurs at higher temperature.
Exp409	12/22/14	None	LANL SA mix w/out liquid	Compare to LANL SA mix w/liquid and WB-4 mix w/out. Appearance of boiling, perhaps from water from Mg nitrate.
Exp410	12/23/14	None	LANL WB-4 mix w/out water, Pb, or Cr	Same as Exp404, but 2°C/min.
Exp411	1/6/15	None	LANL WB-4 mix w/out water, Pb, or Cr	Same as Exp404 and Exp410, but 1°C/min.

2. Results and Observations

Exp386

Exp386 consisted of Swheat and water and was sealed. As shown in Figure 1, the pressure and temperatures increased until about 250°C and 120 psig, at which point the pressure held steady while the temperatures indicated an exothermic event. The source of this event is unknown. Subsequently, the pressure exceeded the measurement range, causing the pressure signal to stop rising at about 2500 psi. The vessel seal subsequently failed, resulting in steam escaping rapidly, as shown in Figure 2. During the cool down, a large endothermic process occurred, the source of which is unknown.

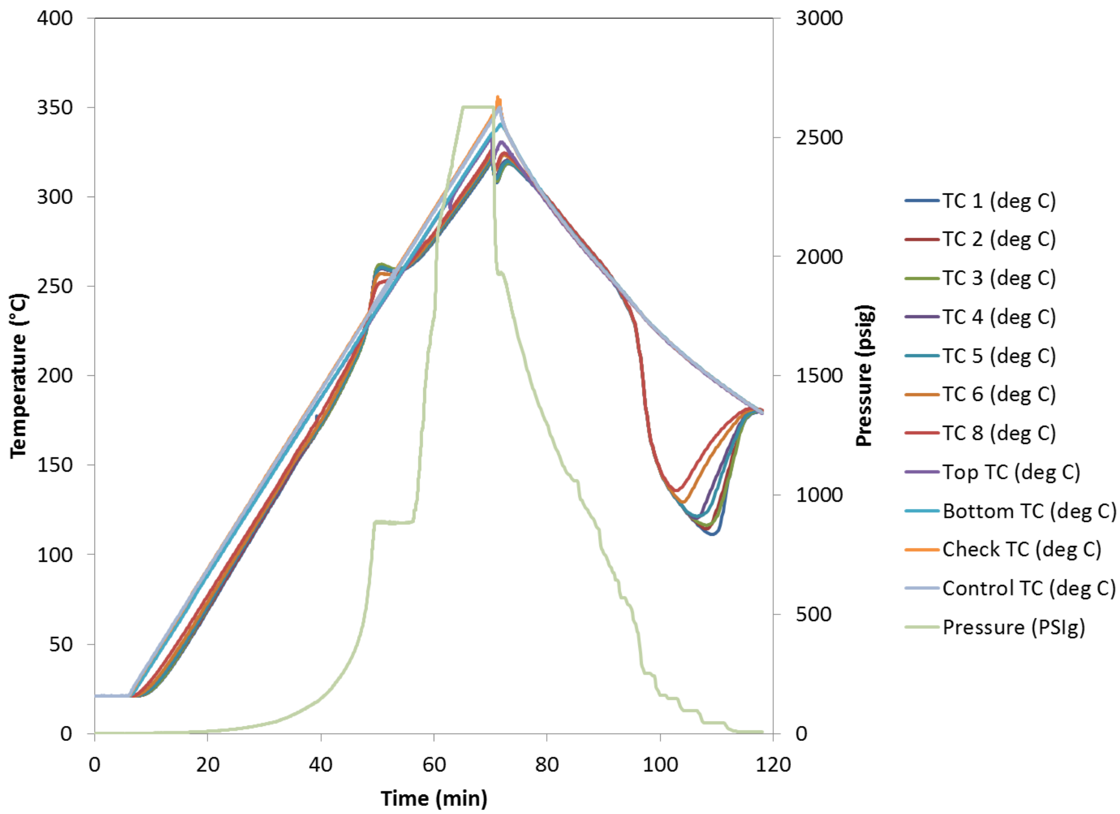


Figure 1. Exp386 temperature and pressure data. Contents were Swheat and water. The vessel was sealed.

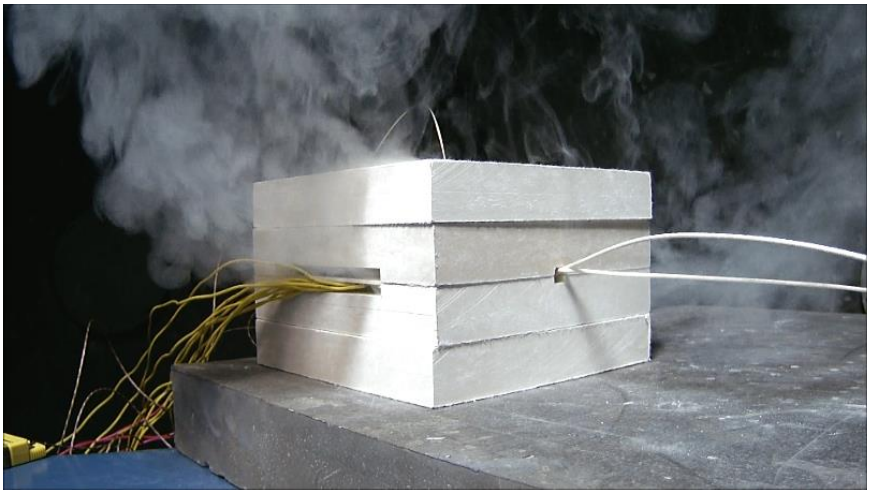


Figure 2. Exp386 video frame showing steam escaping after vessel seal failure.

Figure 3. Exp386 post-test debris.

Figure 3 shows the contents of the vessel after the experiment. The charred remnants indicate that the Swheat was oxidized despite having no exposure to air.

Exp387

Figure 4 shows temperature data from Exp387. This test was run at 2°C/min to reduce the effect of the initial ramp transient at temperatures at which a reaction between the Swheat and water was hypothesized. Because this test was vented, the vaporization of water is apparent at the expected temperature for Albuquerque elevation, about 95°C. After the water was fully vaporized, the temperatures rose to the boundary temperature and exhibited a small exotherm, after which no further reactions were evident. No thermal event associated with absorption of water by the Swheat was observed below the boiling point of water.

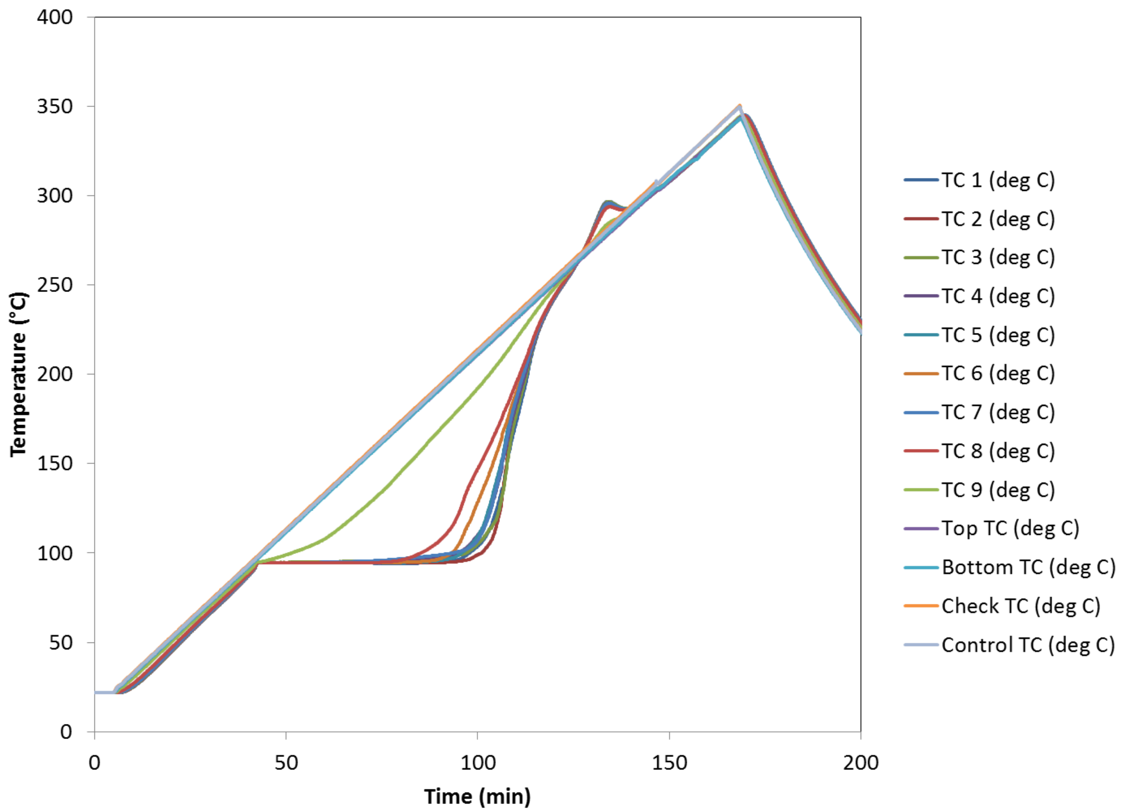


Figure 4. Exp387 temperature data. Contents were Swheat and DI water. The heating rate was 2°C/min.

Figure 5 shows the same sort of oxidative charring that occurred in Exp386.

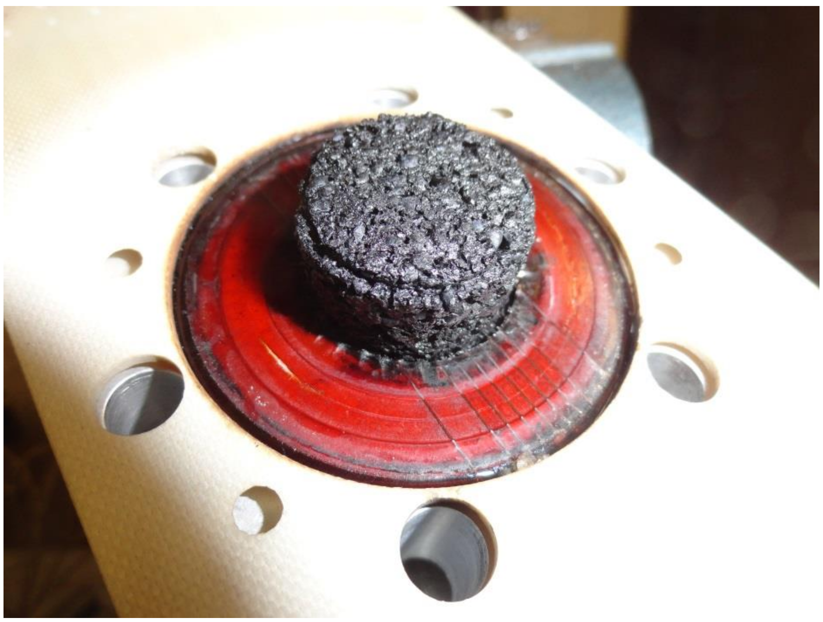


Figure 5. Exp387 post-test residue.

Exp388

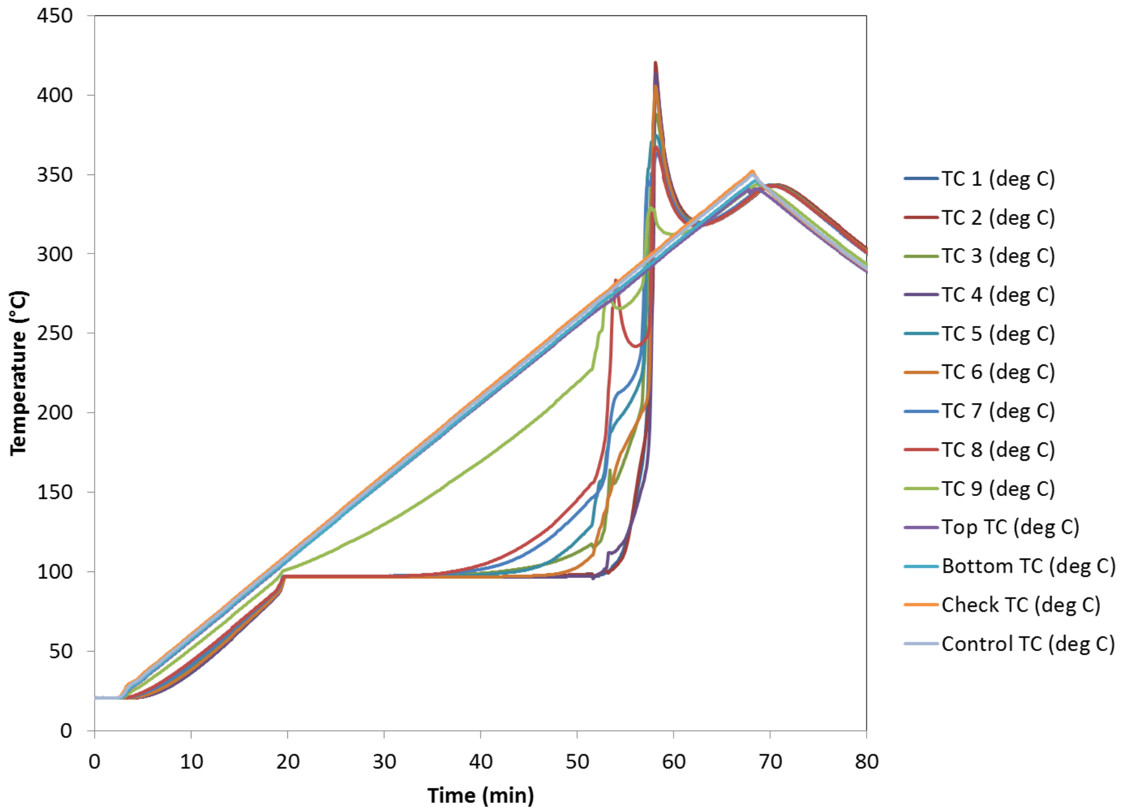


Figure 6. Exp388 temperature data. Contents were neutralized acid and Swheat.

Figure 6 shows temperature data from Exp388. Exp388 contained Swheat and neutralized acid. It was vented and run at 5°C/min. It exhibits exothermic activity that starts at the end of the water vaporization, slows, and then accelerates again after the water is vaporized. The internal temperatures remained at about 97°C during the water vaporization, slightly higher than in Exp387 because of dissolved TEAN from the neutralized nitric acid. The two exothermic events correspond to exhaust jets in the video, as shown in Figure 7. Before, between, and after the jets, a stream of smoke or steam was visible, but not during most of the water vaporization.

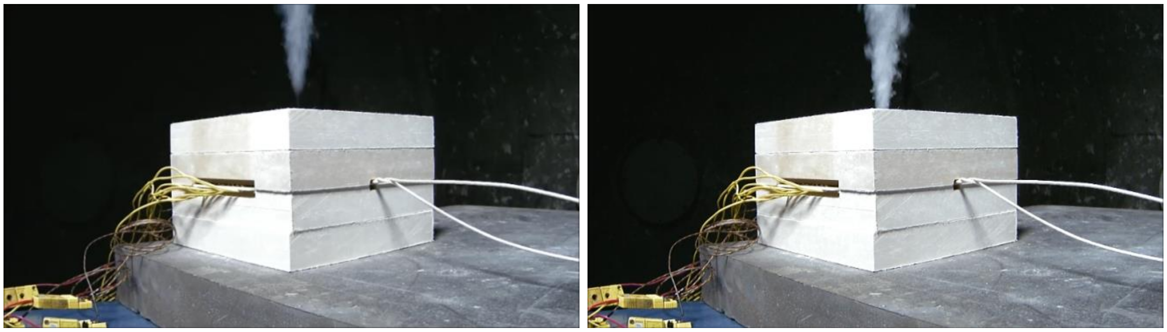


Figure 7. Frames from Exp388 video showing two jets.

Figure 8. Exp388 post-test residue.

Figure 8 shows the post-test contents of the experiment. Although charred, the substantial amount of material remaining indicates that the exothermic event does not consume all of the reactants.

<u>Exp389</u>

Figure 9 shows temperature data from Exp389. This test contained Swheat and water, like Exp387, but used the normal 5°C/min ramp rate. In comparison to Exp387, there is no exothermic event, until the top of the ramp after the heater power was turned off, demonstrating the effect of heating rate on exotherm temperature. In comparison with Exp388, this demonstrates the effect of neutralized acid (presumably TEAN, in Exp388). The video showed a slow stream of smoke or steam, but no evidence of ignition or burning. With the slower heating rate, the vaporization of water was complete during the heating ramp, and was followed by an exothermic reaction. With the faster heating rate, the heating ramp was over by the time the water was completely vaporized. This also illustrates the significant role of water vaporization in suppressing the effects of exothermic reactions. The internal temperatures remained at about 95°C during the vaporization of water, as in Exp387.

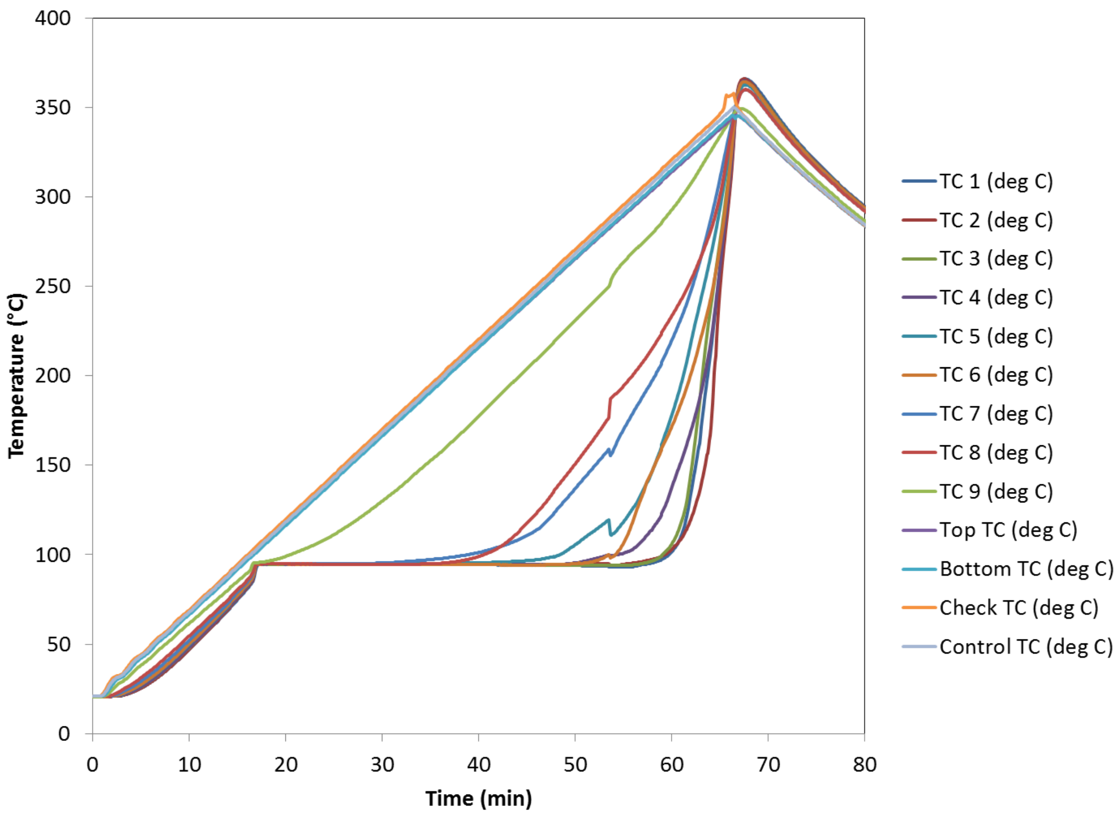


Figure 9. Exp389 temperature data. Contents were water and Swheat.

Figure 10 shows the charred Swheat remaining after Exp389. They are identical in appearance to the remains of the previous tests.

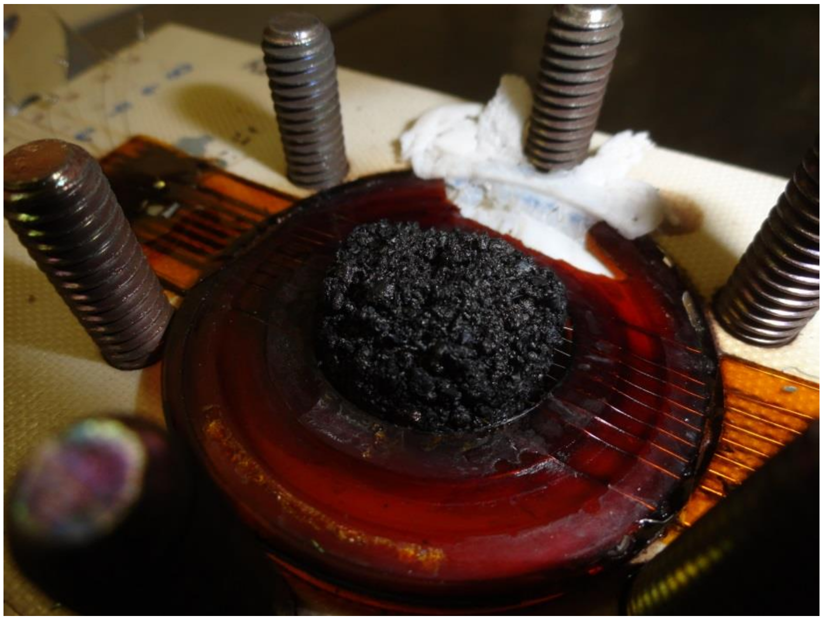


Figure 10. Exp389 post-test residue.

Exp390

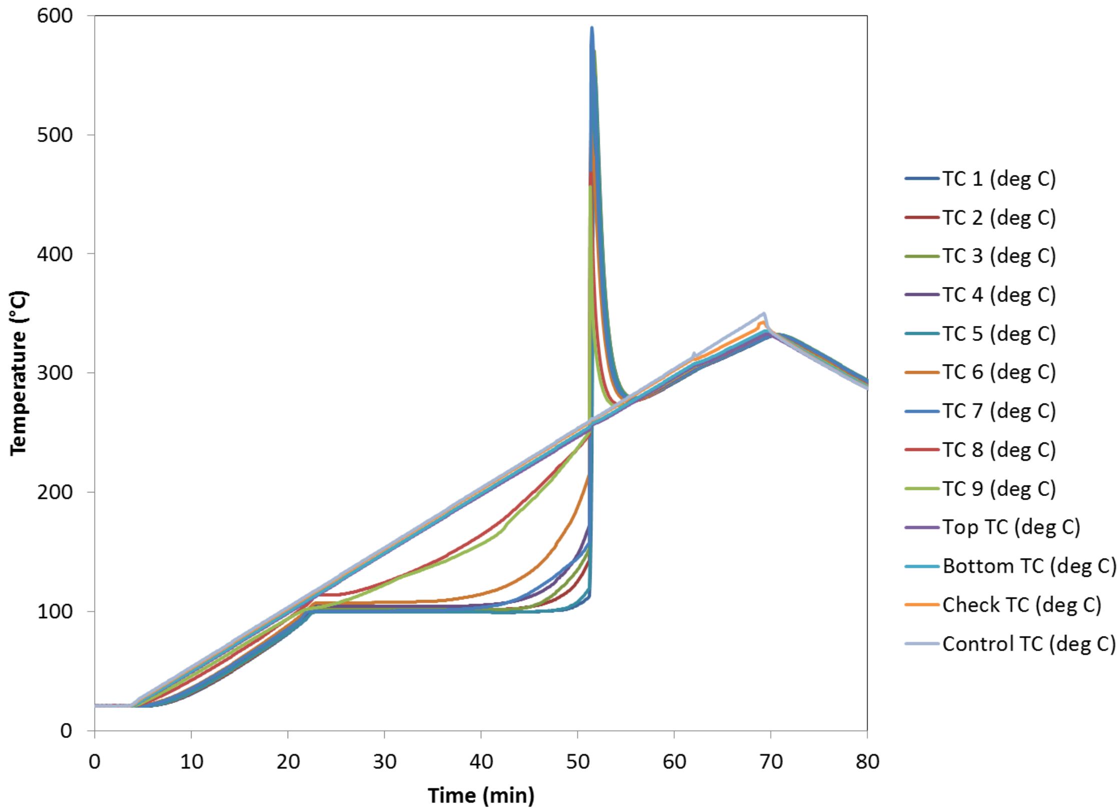


Figure 11. Exp390 temperature data. Contents were neutralized acid, Swheat, magnesium nitrate hexahydrate, and sodium nitrate.

The temperature data from Exp390 shown in Figure 11 show an exotherm after vaporization of water that reaches 600°C, higher than the exotherm in Exp388 and starting at a lower temperature (although this may be related to differing amounts of liquid – the moisture content was about 28% in Exp390 and 48% in Exp388). The exotherm occurs at about 51 minutes, when the boundary temperature is about 258°C, whereas in Exp388 the initial exotherm occurred at about 52 minutes when the boundary temperature was about 270°C but quenched and was followed by a stronger exotherm at 57 minutes when the boundary temperature was about 294°C. The video showed an explosive release followed by a decaying jet that was more energetic than the jets seen in Exp388. These observations suggest that adding sodium and magnesium nitrates enhances reactivity relative to Swheat and neutralized acid, although this may be due to the simultaneous reduction in the amount of liquid. The post-test debris shown in Figure 13 is essentially identical to previous tests.

Except for the outer two thermocouples, which are often dominated by the vessel wall, the internal temperatures ranged between 100°C and 107°C during the vaporization of water. The shift upward relative to Exp387, Exp388, and Exp389 is apparently due to dissolved Mg and Na nitrate salts, in addition to TEAN.

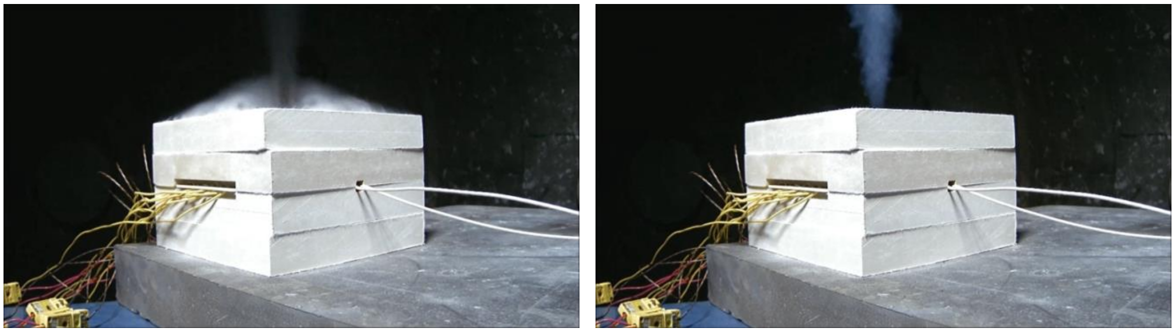


Figure 12. Image from video of Exp390. Left: explosive event accompanied by loud report, and right: decaying jet that followed the explosive event.

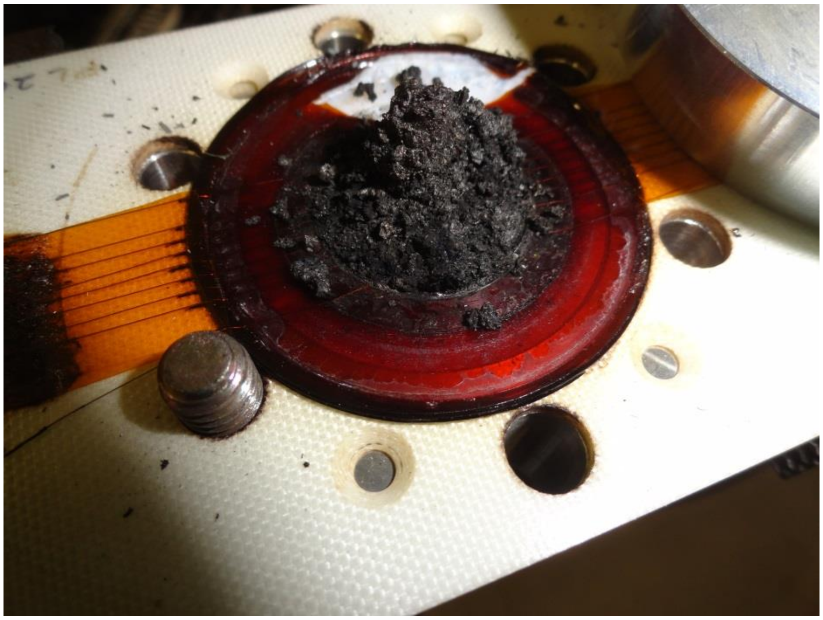


Figure 13. Exp390 post-test residue.

<u>Exp391</u>

Exp391 was a test of compatibility between under-neutralized nitric acid and Swheat and Na and Mg nitrates, and between the mixture and the aluminum vessel. This was done prior to testing this mixture in a closed vessel, and to determine if reaction between the acid (in the presence of the Swheat and nitrate salts) and the aluminum vessel could affect results. Part of the vessel was coated with M-Bond 610 to evaluate the effectiveness of this coating in protecting the aluminum. The temperature was first ramped to 100°C, to accelerate reactions, and after some time at 100°C, was raised to 150°C.

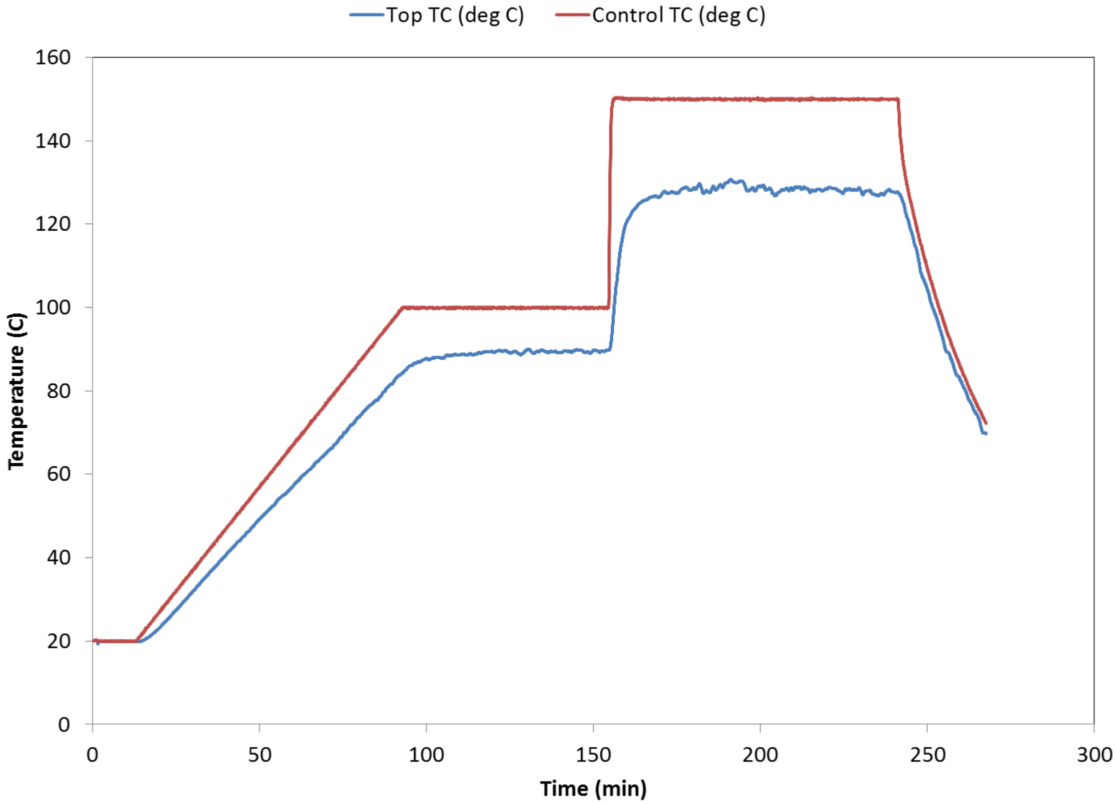
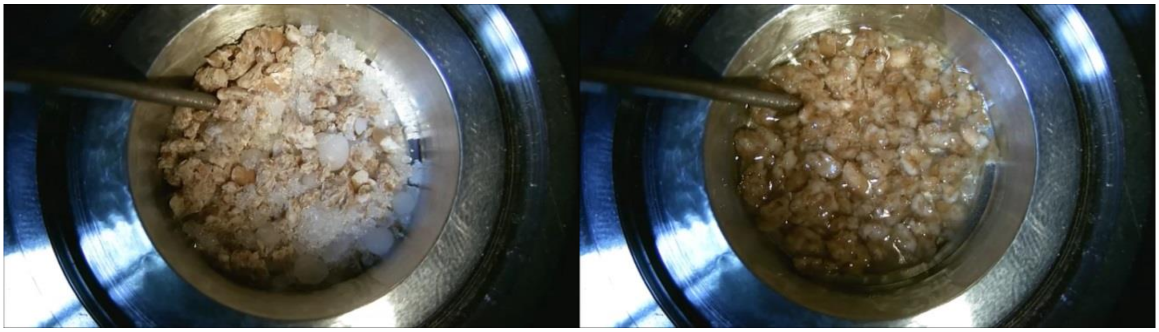


Figure 14. Temperature data from Exp391. This test was a compatibility test of Na and Mg nitrates with under-neutralized acid, and with the aluminum vessel. The "top" temperature was measured by a thermocouple stuck into the reactant mixture, which is cooler than the control temperature because of heat losses to the environment.

The results of Exp391 indicated no noticeable gas generation and no damage to the aluminum vessel at any temperature up to 150°C. Most of the liquid evaporated, but the mixture remained moist.



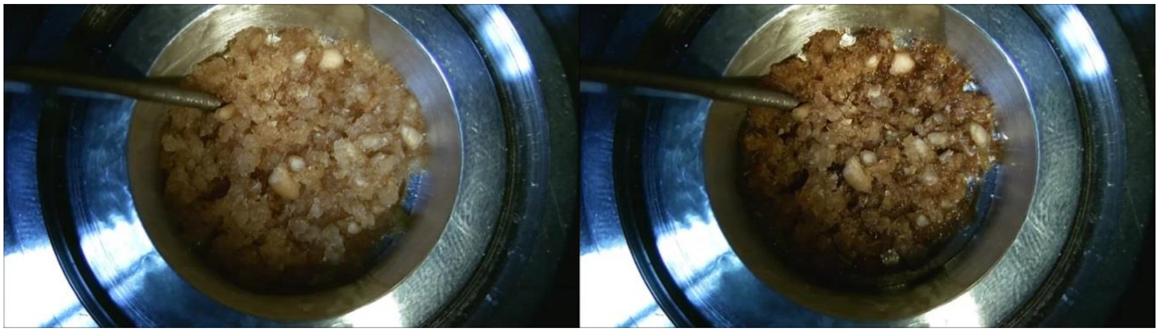


Figure 15. Images taken from video of Exp391. From left to right, top to bottom: before under-neutralized nitric acid was added, immediately after the liquid was added, 92.8 minutes into the test, and 154 minutes into the test.

Exp392

Exp392 used the same mixture as Exp391 – Swheat, Na and Mg nitrates, and under-neutralized nitric acid. In comparison with Exp390, Exp392 was intended to demonstrate if under-neutralization would affect reaction rates.

The temperature data from Exp392 shown in Figure 16 exhibit two exotherms like Exp388, with one occurring toward the end of the vaporization of water and the second occurring after the water is entirely vaporized. The first event, despite appearing sudden in the temperature data, was relatively mild in the video. The second event started with an explosive release, followed by a decaying jet.

Similar to Exp390, the internal temperatures remained between about 102°C and 108°C during the vaporization of water, due to dissolved solids.

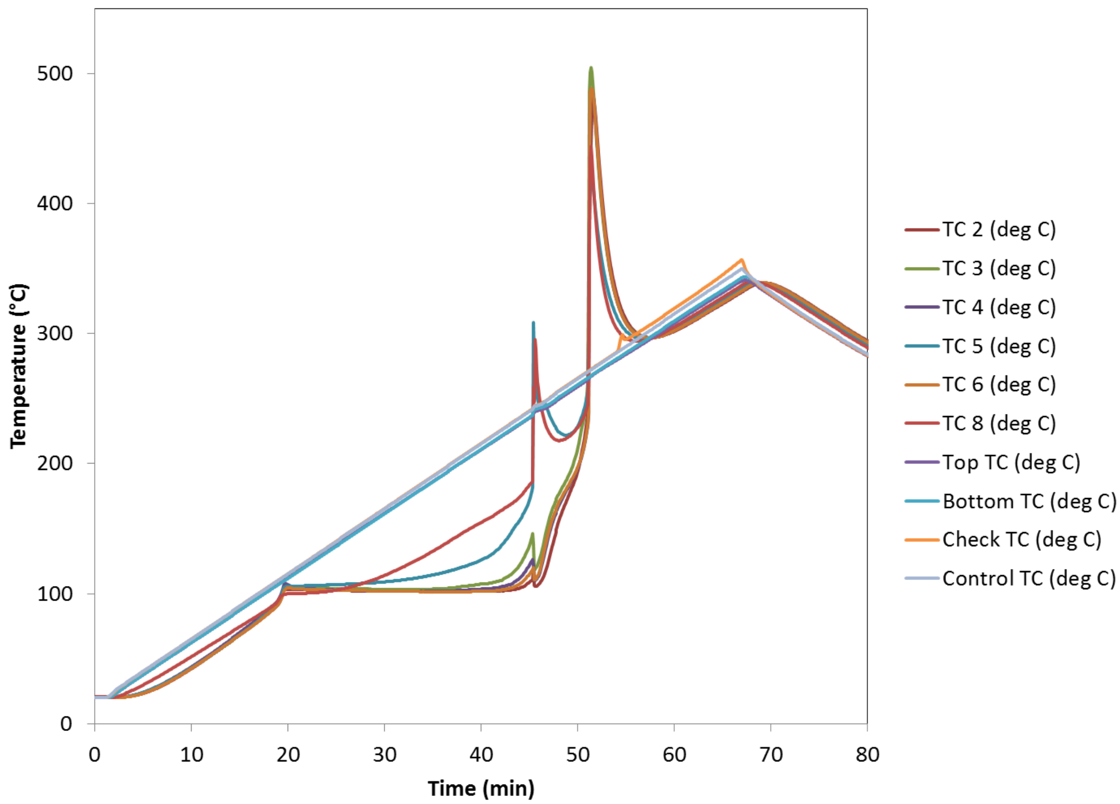


Figure 16. Exp392 temperature data. Contents were under-neutralized acid, Swheat, magnesium nitrate hexahydrate, and sodium nitrate.

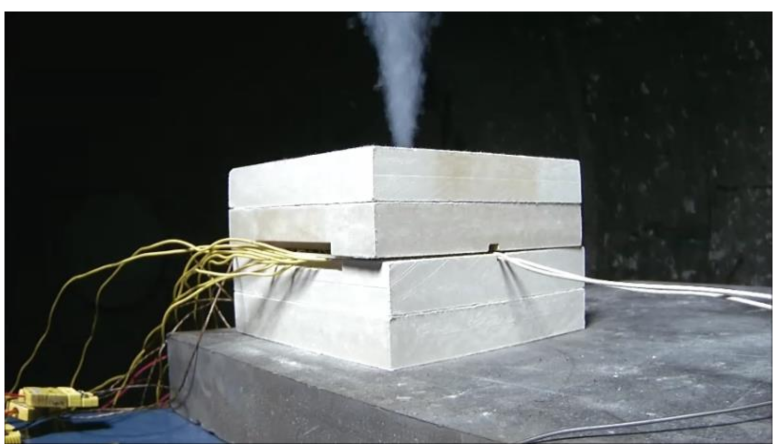


Figure 17. Image from video of Exp392. This image was taken during the first of two exothermic events.

Figure 18 shows the post-test debris from Exp392 and is similar to previous tests. Exp392 was more energetic than Exp388 (Swheat and neutralized acid) but also exhibited two exothermic events, whereas Exp390 (Swheat, nitrate salts, and neutralized acid) was energetic but only exhibited one exothermic event. This suggests that the difference between one or two events is coincidental, and supports the conclusion that nitrate salts increase the violence of reaction (but does not rule out the possibility that the increased reactivity is actually due to lower liquid content). There is no apparent difference between neutralized acid and under-neutralized acid.

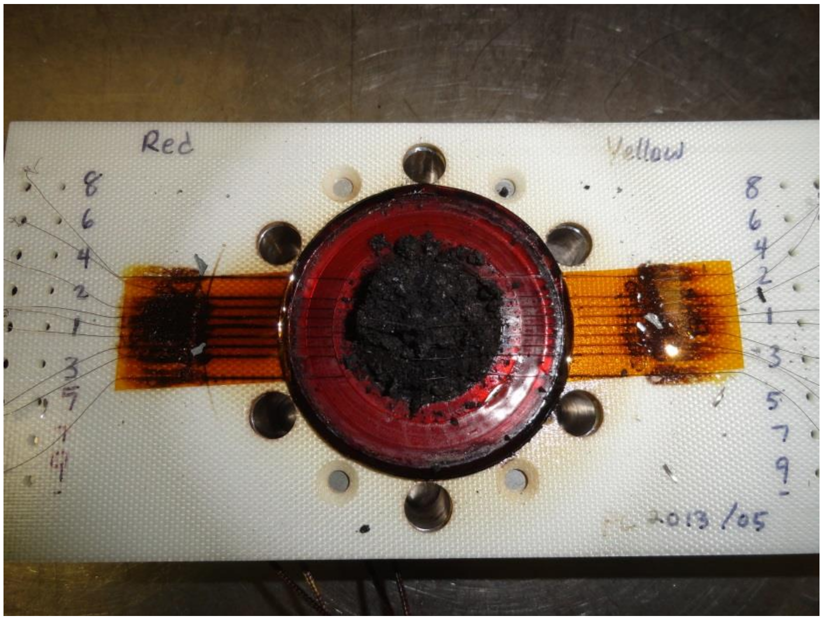


Figure 18. Exp392 post-test residue.

<u>Exp394 and Exp395</u>

Exp394 and Exp395 were intended to evaluate the effect of over-neutralized nitric acid, relative to under-neutralized nitric acid used in Exp392 and neutralized acid used in Exp390, but were performed with about three times as much nitrate salt as intended, due to use of an erroneous density measurement. Exp395 was performed to repeat Exp394 because of observations in Exp394 that appeared anomalous. These two tests were intended to be identical, and the results are virtually the same.

The temperature data show instead of a clear vaporization process as in previous steps, only a slight endothermic deviation of the internal temperatures relative to the external temperatures. As the internal temperatures begin to curve upward (in Exp394, the internal temperatures exceed the boundary temperatures), indicating the beginning of an exothermic process, the temperatures suddenly drop about 100°C. After a few minutes, during which the internal temperatures are a little above 100°C suggesting vaporization of water, the internal temperatures rise rapidly, but do not exhibit a substantial exotherm, in that they do not exceed the boundary temperatures.

The video provides evidence of what causes this behavior. The sudden temperature drop is accompanied by an explosive release. This indicates that the vent was clogged prior to the release. Pressure built inside the vessel as water vaporized, suppressing the vaporization. The pressure increased with the temperature along with gas generation from reactions, finally resulting in failure of the clog and release of pressure. When the pressure was released, the water rapidly vaporized. When the moisture was gone, decomposition occurred rapidly, resulting in another explosive event. In this case the event was strong enough to launch the top insulation block off the apparatus. It is not clear why the temperature data do not show an accompanying exothermic event.

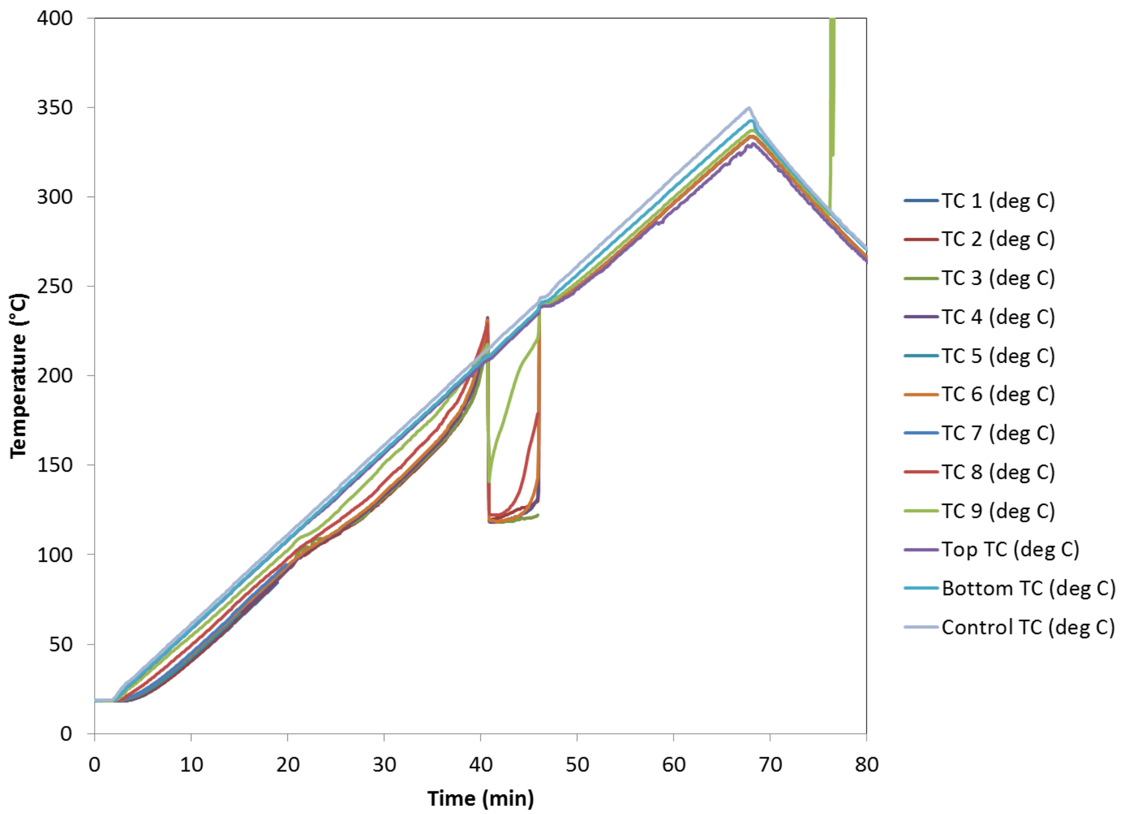


Figure 19. Exp394 temperature data. Contents were over-neutralized acid, Swheat, magnesium nitrate hexahydrate, and sodium nitrate. The amount of nitrate salts was about three times more than should have been.

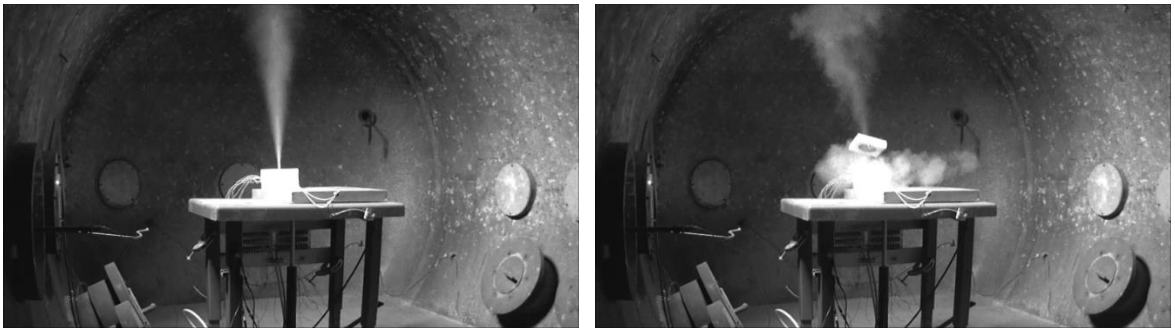


Figure 20. Images from video of Exp394. Left: explosive event at 40.7 minutes. Right: energetic event at 45.9 minutes, showing the top layer of insulation being blown off.

The beginning of exothermic activity around 200°C indicates that this is the temperature of onset of exothermic reaction at this heating rate at this scale, with this mixture, when the system is sealed so that water cannot escape. The peculiar behavior is probably strictly related to a temporarily sealed system.

Figure 21. Exp394 post-test residue, showing the top of the vessel with expelled material.

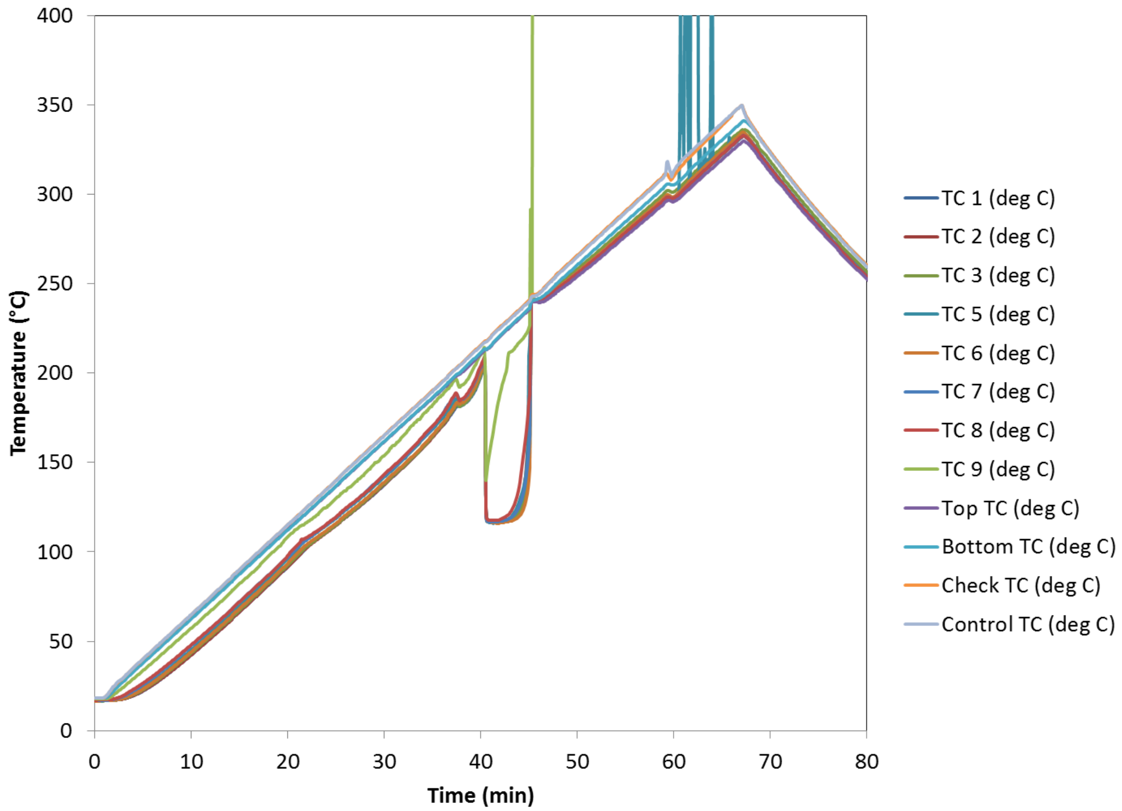


Figure 22. Exp395 temperature data. Contents were over-neutralized acid, Swheat, magnesium nitrate hexahydrate, and sodium nitrate. The amount of nitrate salts was about three times more than should have been.

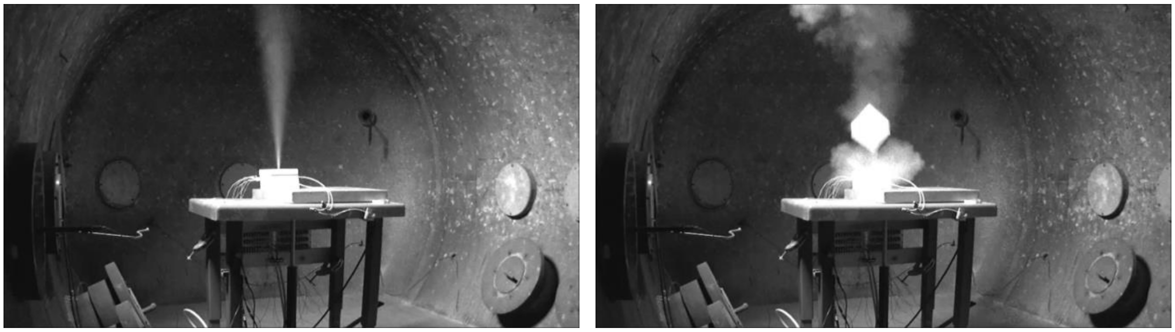


Figure 23. Images from video of Exp395. Left: explosive event at 40.5 minutes. Right: energetic event at 45.1 minutes, showing the top layer of insulation being blown off.

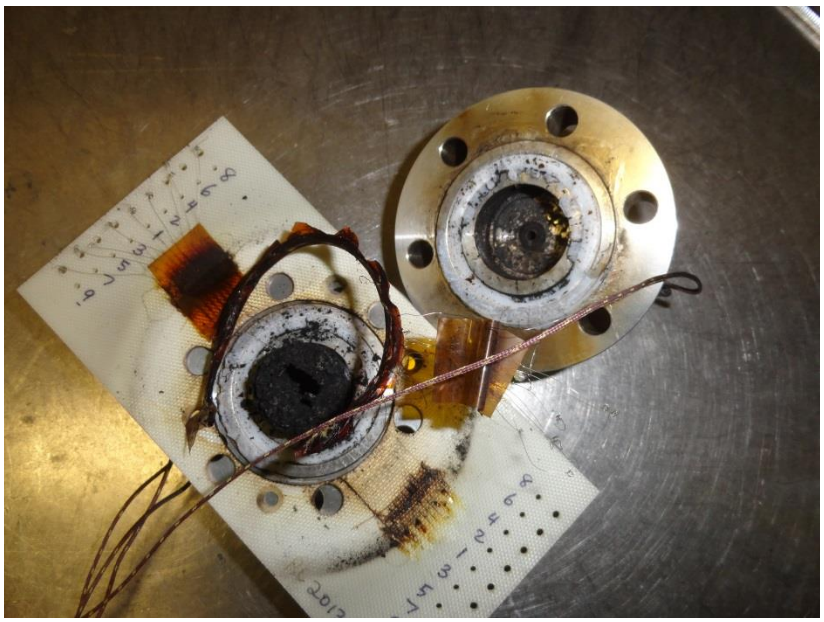


Figure 24. Post-test debris from Exp395. The Teflon O-rings appear to be intact, indicating that the violent release that launched the top insulation block occurred only through the top vent.

<u>Exp396</u>

Exp396 was the same as Exp394 and Exp395 (over-neutralized acid, Swheat, and Mg and Na nitrates) except with the correct amount of nitrate salts (same as Exp390 and Exp392). As seen in Figure 25, the effect was that the normal water vaporization returned followed by an exothermic event. In fact, a closer look at the data and the video indicates that there were two exothermic events, although the first was explosive and the second was gradual. These results are virtually identical to Exp390 (Swheat, neutralized acid, and nitrate salts), and similar to Exp392 (Swheat, under-neutralized acid, and nitrate salts). Both Exp392 and Exp396 exhibited two exothermic events, although they were different in timing. The post-test debris shown in Figure 27 show that as usual, charred material remained after the test.

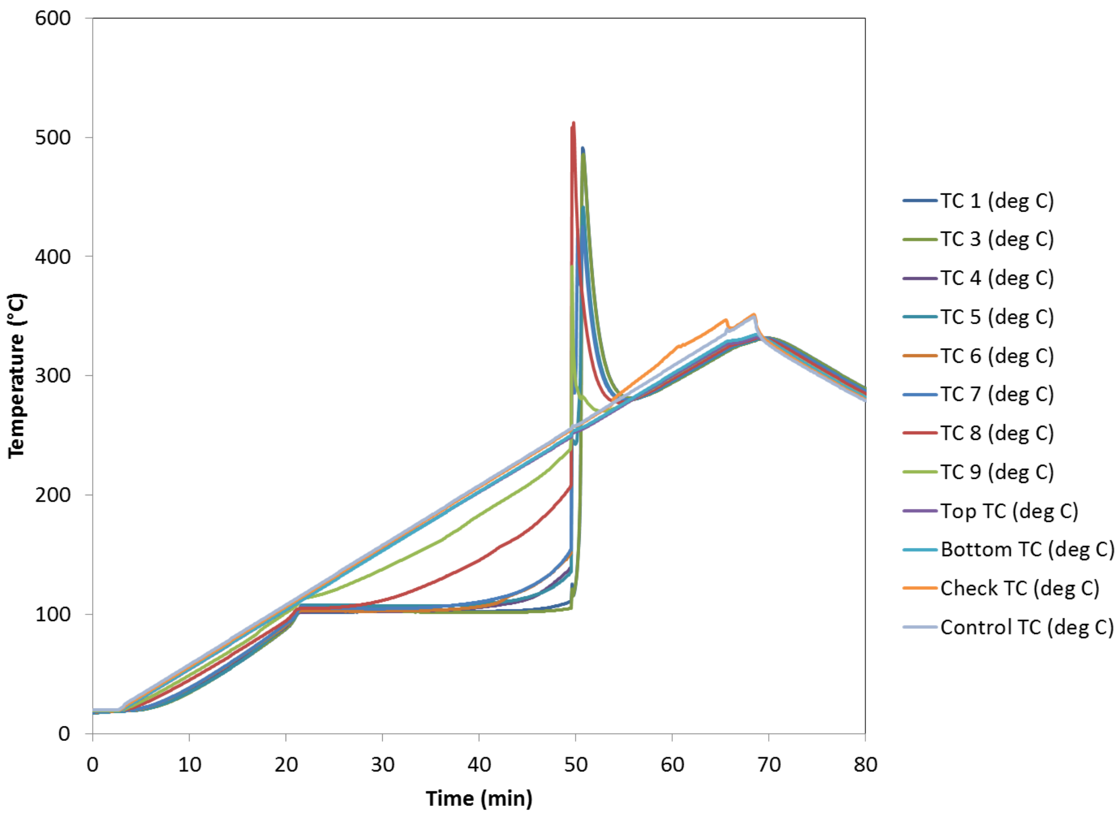


Figure 25. Exp396 temperature data. Contents were over-neutralized acid, Sweat, magnesium nitrate hexahydrate, and sodium nitrate.

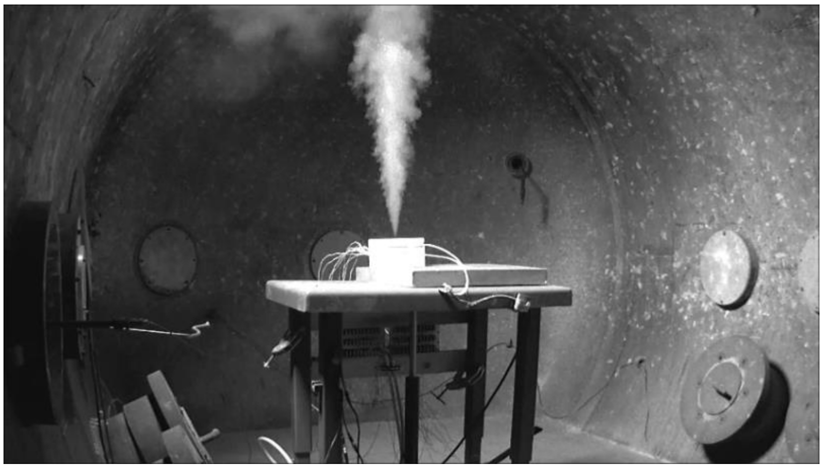


Figure 26. Image from video of Exp396.

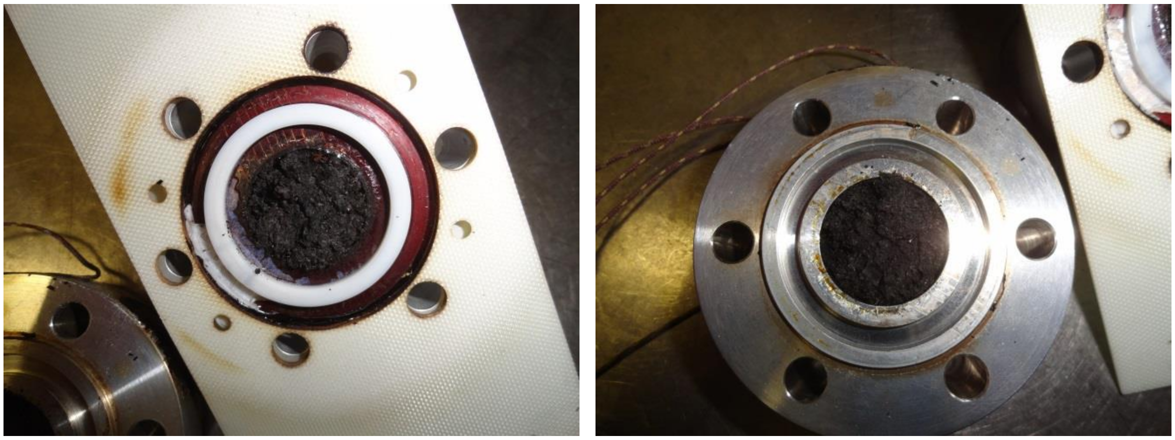


Figure 27. Post-test debris from Exp396.

<u>Exp397</u>

Exp397 was a compatibility test, similar to Exp391, using a mixture based on the LANL Stream Analyzer predicted mixture. Table 2 lists the constituents and mass fractions in the original LANL Stream Analyzer mixture, and a simplified version used in these tests. The simplified version omits trace metals, liquid water, and nitric acid.

Table 2. LANL Stream Analyzer mixture and simplified version.

Substance	Original Mass Fraction	Simplified Mass Fraction
$Al(NO_3)_3$*$9H_2O$	0.02374	0.02420
$Ca(NO_3)_2$*$4H_2O$	0.09454	0.09639
KNO_3	0.02072	0.02112
$Cr(NO_3)_3$*$9H_2O$	0.001243	0.001264
$Fe(NO_3)_3$*$9H_2O$	0.06443	0.06570
H_2O-HNO_3-Al-Ca-Cr-Fe-Mg-Ni	0.001935	
$Mg(NO_3)_2$*$6H_2O$	0.6220	0.06341
HNO_3	0.01531	
$NaNO_3$	0.1364	0.1391
NaF	0.001824	0.001860
$Ni(NO_3)_2$*$6H_2O$	0.0006129	0.0006280
$Pb(NO_3)_2$	8.529e-5	8.856e-5
$(COOH)_2$	0.01524	0.01554
H_2O	0.001935	

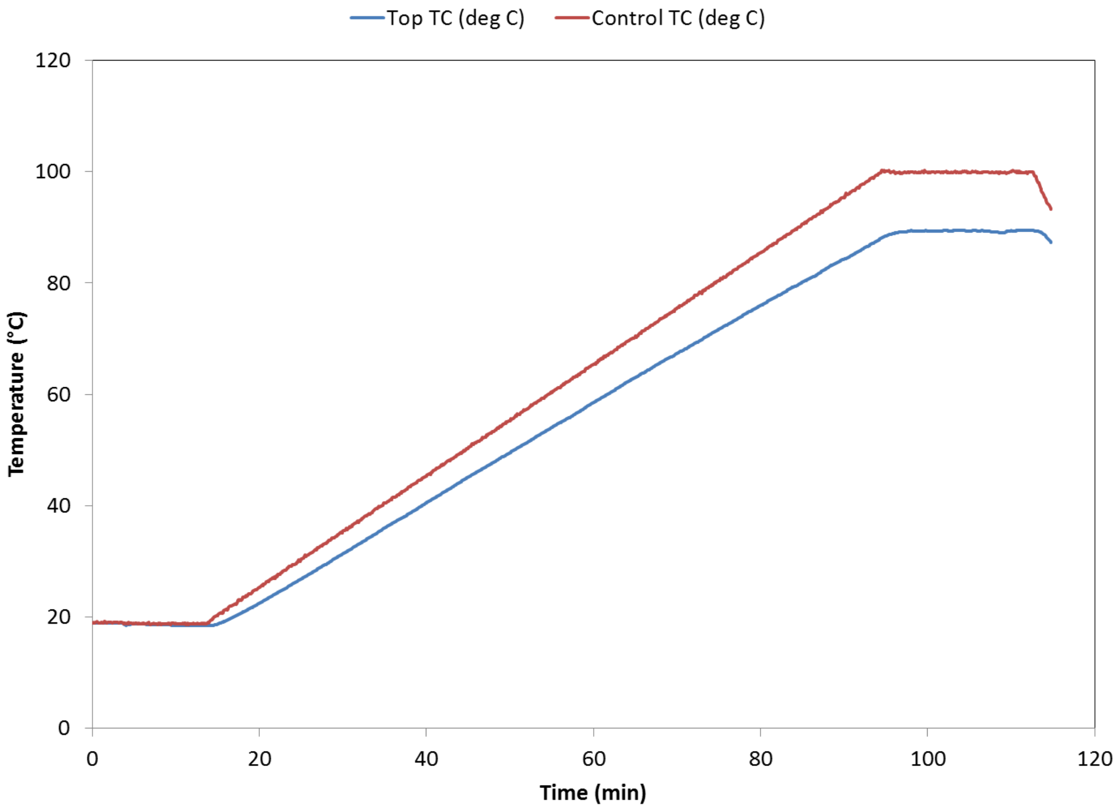


Figure 28. Temperature data from Exp397. This was a compatibility test of LANL SA mixture, Swheat, and over-neutralized nitric acid.

Figure 29. Images from video of Exp397. From left to right, top to bottom: before over-neutralized nitric acid was added, immediately after addition of liquid, 95 minutes into the heating, and 112 min into the test.

Exp398

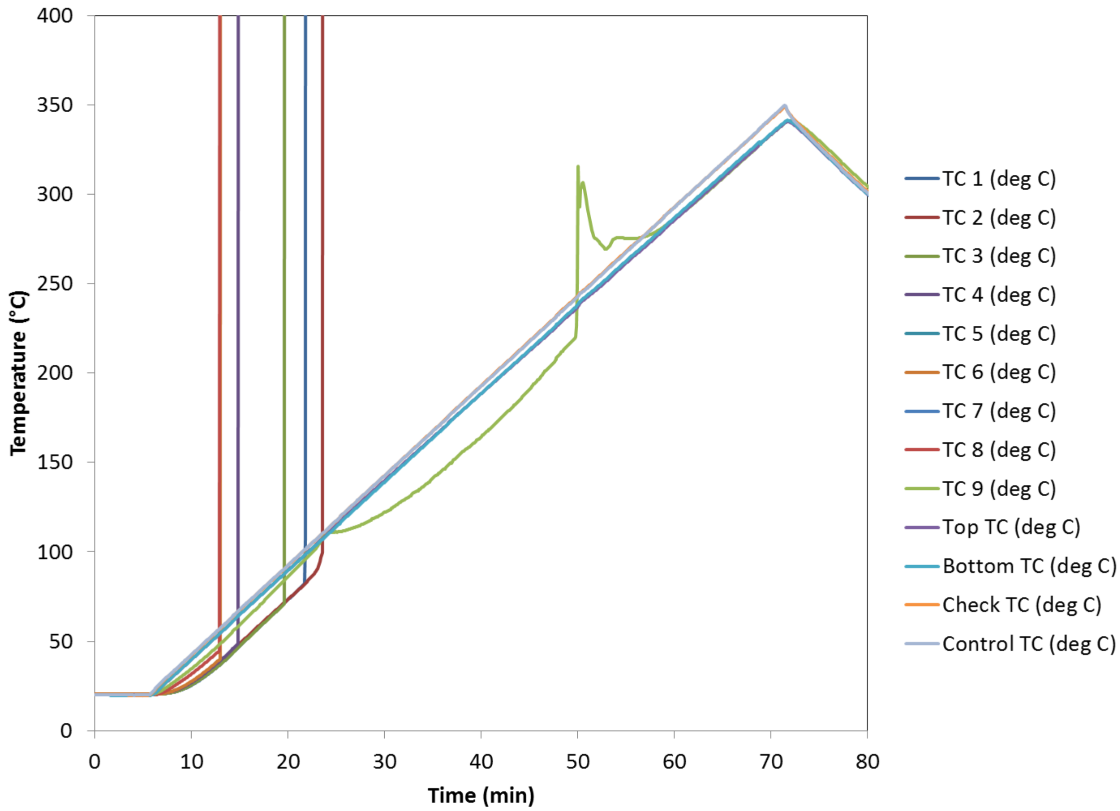


Figure 30. Exp398 temperature data. Contents were over-neutralized acid, Swheat, and the LANL SA mix.

Exp398 was performed with a mixture of nitrate salts and the LANL SA mix, and was intended to show whether any of the materials would result in a qualitatively different result from the same with magnesium and nitrate salts alone. Figure 30 appears very different from the temperature data from other tests, but it is difficult to determine how meaningful these differences are because most of the internal thermocouples failed before the beginning of the water vaporization. The only surviving thermocouple, TC8, is relatively close to the edge and behaved similar to other tests. It is possible the water vaporization occurred as usual. The failure of most of the thermocouples could be an effect of one or more of the materials used, as reactions with the thermocouple wires could cause them to break, or it could have been due to movement of the salts. An exothermic event occurred at a similar time and temperature as in previous tests, where the vaporization of water would be complete. The video showed that the exothermic event was accompanied by a jet which at one point accelerated to a high rate but which for the most part was sustained over a long period with little violence. The net result seems to indicate that the large mixture of salts did not result in a substantially different result, and may have been somewhat less energetic than the magnesium and nitrate salt mixture, perhaps simply because most of the added materials did not contribute to the reactivity and diluted those that did.

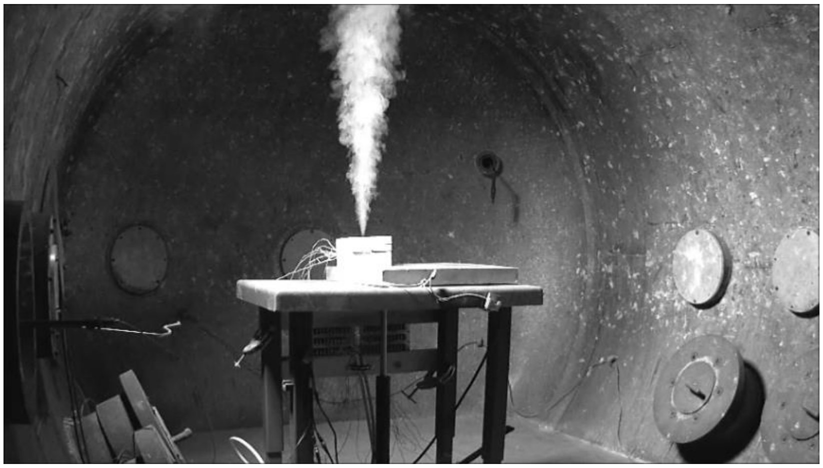


Figure 31. Image from video of Exp398 taken at around 50 minutes.

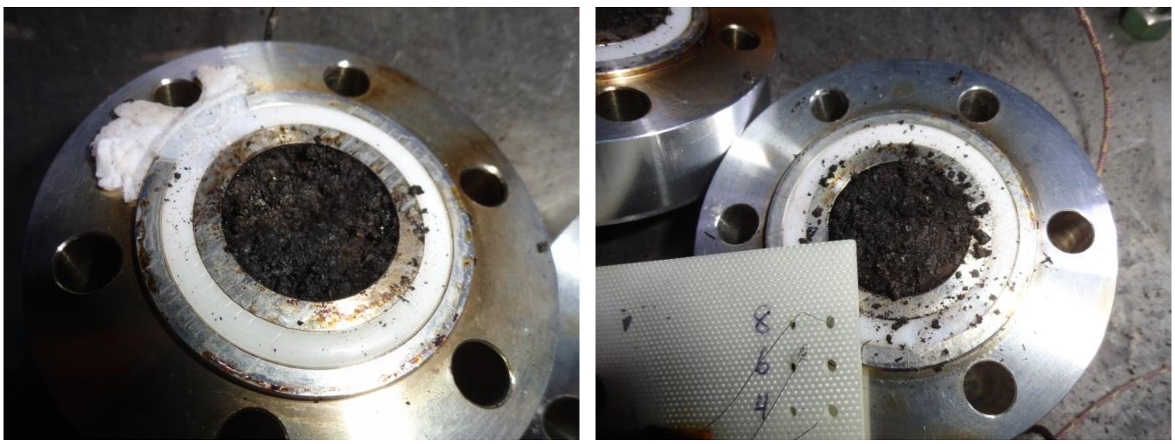


Figure 32. Post-test debris from Exp398.

<u>Exp399</u>

Exp399 used the same mixture of over-neutralized nitric acid, Swheat, and Mg and Na nitrates as Exp396. To test the hypothesis that water suppresses reactions that may occur at temperatures below 100 C, Exp399 was preceded by pulling a vacuum for 200 minutes, during which the vacuum was measured at 10 mTorr. The results show that the water was not removed, and in comparison with Exp396, the results were very similar suggesting that little water was actually removed.

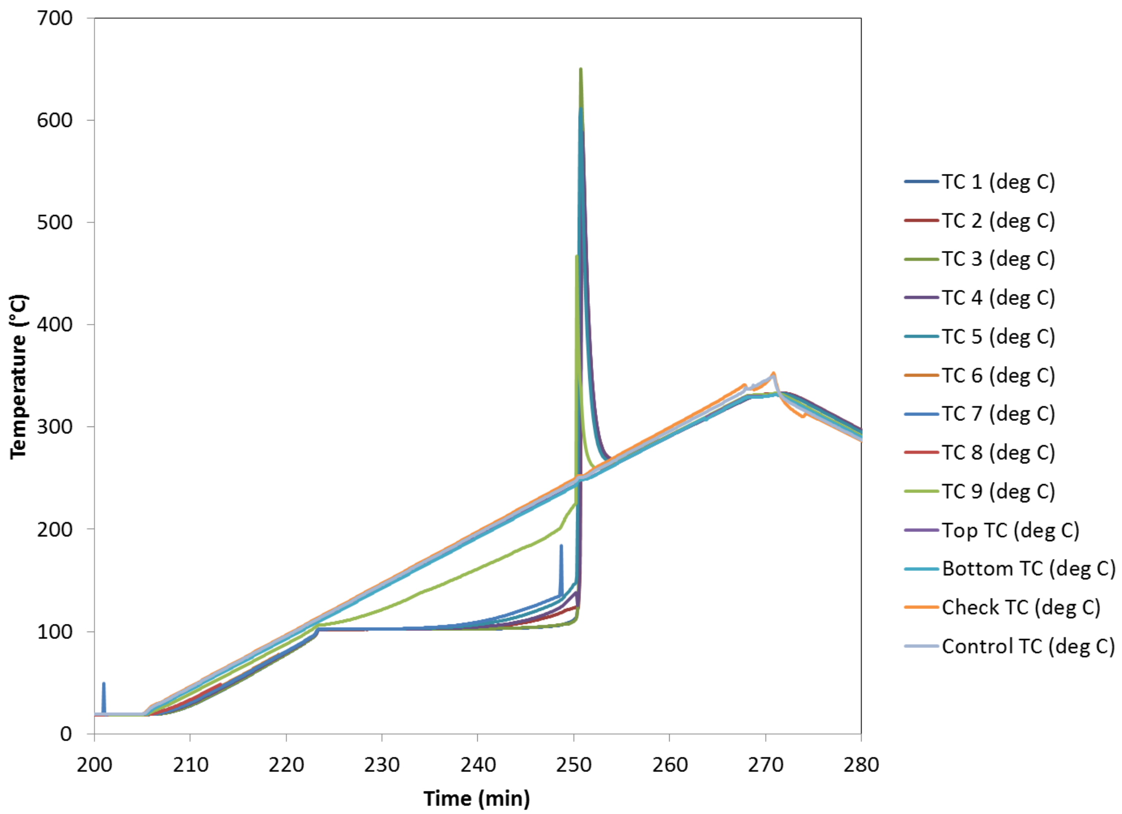


Figure 33. Temperature data from Exp399. Contents were Swheat, over-neutralized acid, Na nitrate, and Mg nitrate.

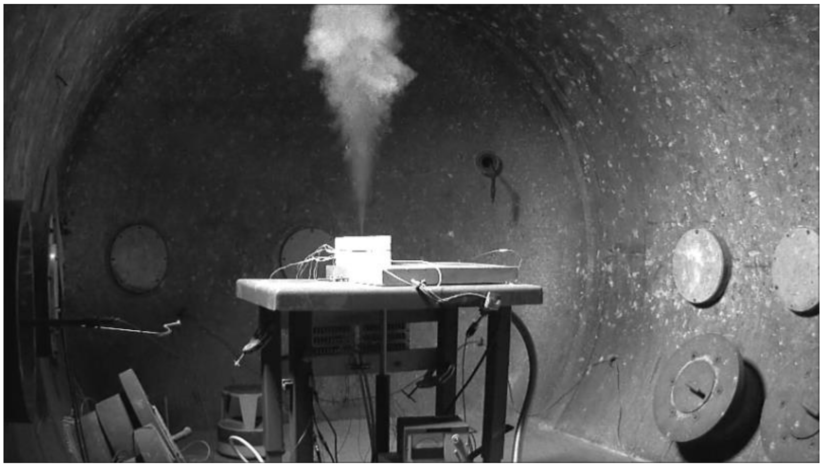


Figure 34. Image from Exp399 video taken around 245 minutes.

The video of Exp399 shows a rapidly increasing jet followed by a number of small sudden loud reports.

<u>Exp400</u>

Exp400 was a series of attempts to ignite the remains of Exp397 including with a nichrome wire and with a glow plug. None worked.

Exp401

In another attempt to investigate the effect of removing water, Exp401 consisted of a ramp-and-hold at 105°C. It was heated to 105°C because the vaporization process was observed to occur between 100°C and 105°C in previous tests, presumably due to dissolved salts in the water. Based on the water vaporization observed in other tests, the water was expected to boil off rapidly and the dry material was expected to ignite soon after. After about 4 hours, the internal temperatures approached the boundary temperature but did not show any signs of exothermic reaction, so the heat was turned off. The next day, the test was continued, and after another 4 hours, the temperature was ramped again at 5°C/min until ignition.

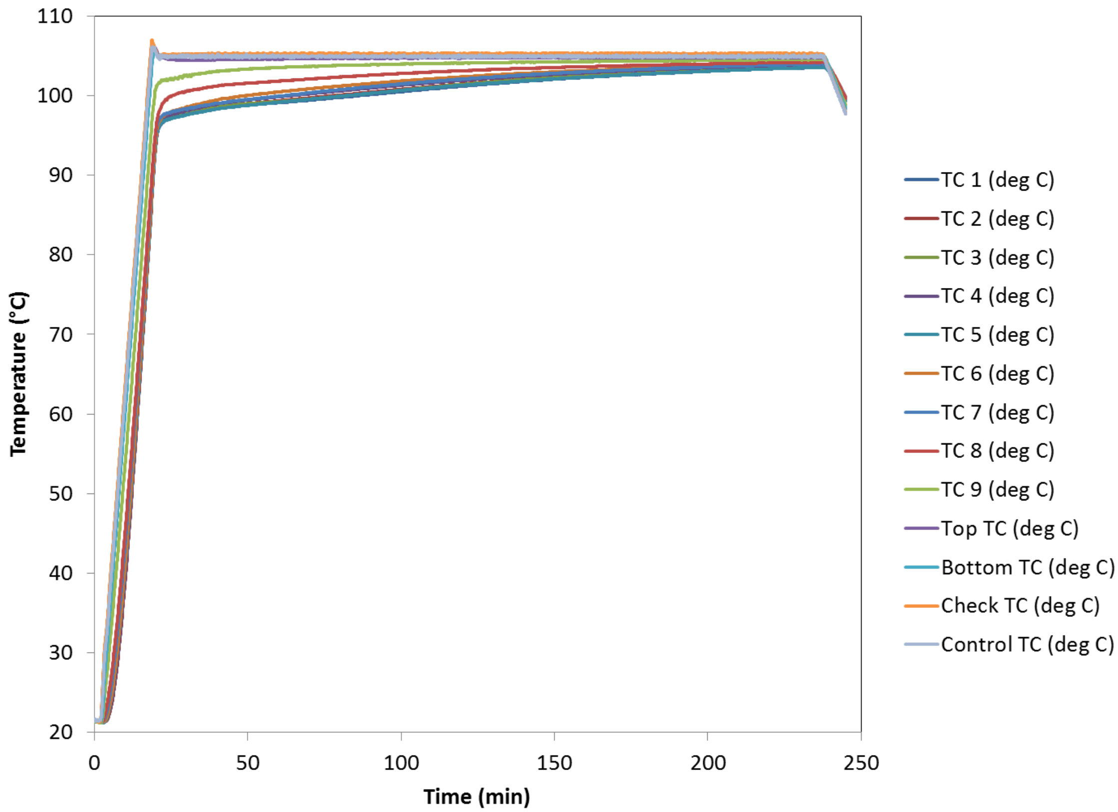


Figure 35. Exp401 initial ramp and hold at 105°C.

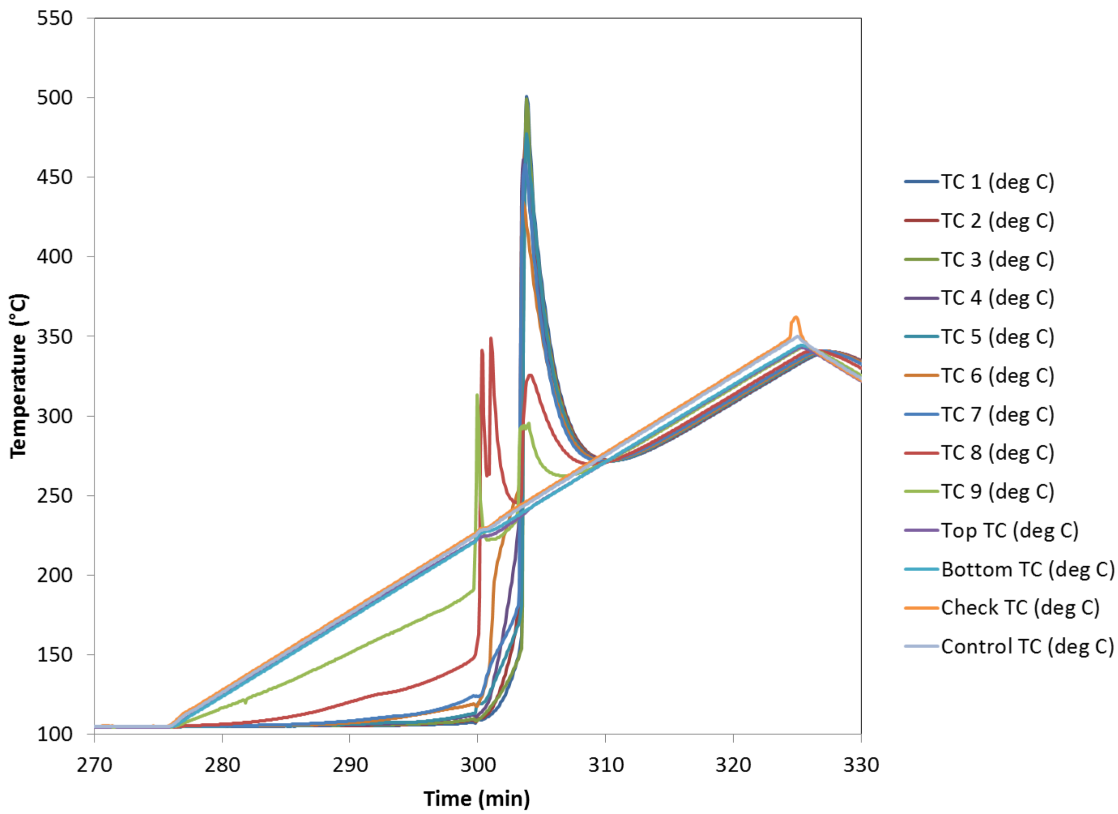


Figure 36. Exp401 second part - reheated and held at 105°C for about 4 hours, then heated at 5°C/min.

The temperature data in Figure 36 show two strong exothermic events around the end of the water vaporization, and the video shows two corresponding jets, neither of which was particularly violent.

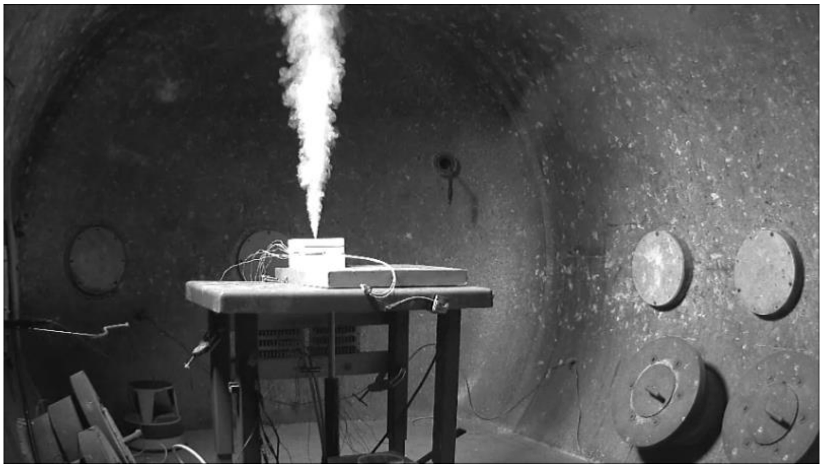


Figure 37. Image from video of Exp401.

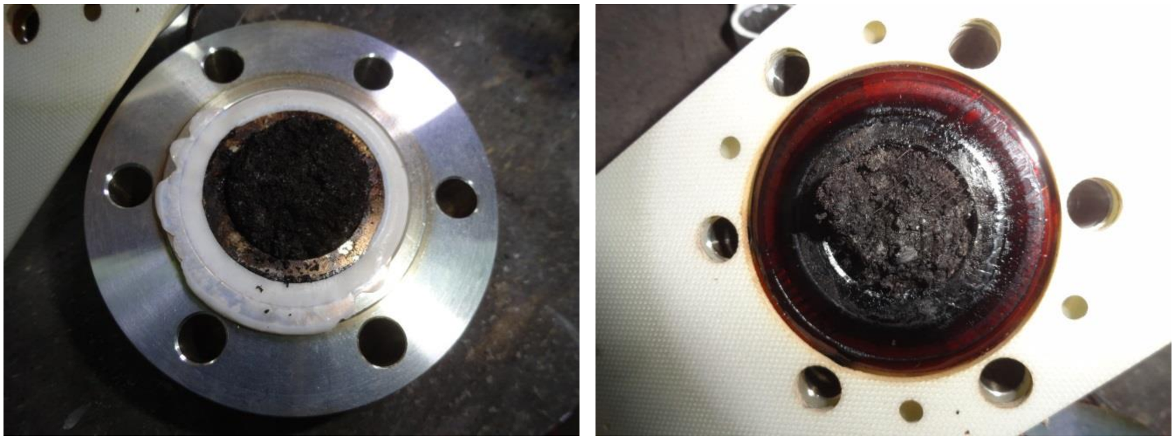


Figure 38. Post-test debris from Exp401.

<u>Exp402</u>

Exp402 was essentially a repeat of Exp401, except at 110°C instead of 105°C. The results were very similar. The water appears to have vaporized, but no exothermic reactions were observed until the temperature was ramped higher.

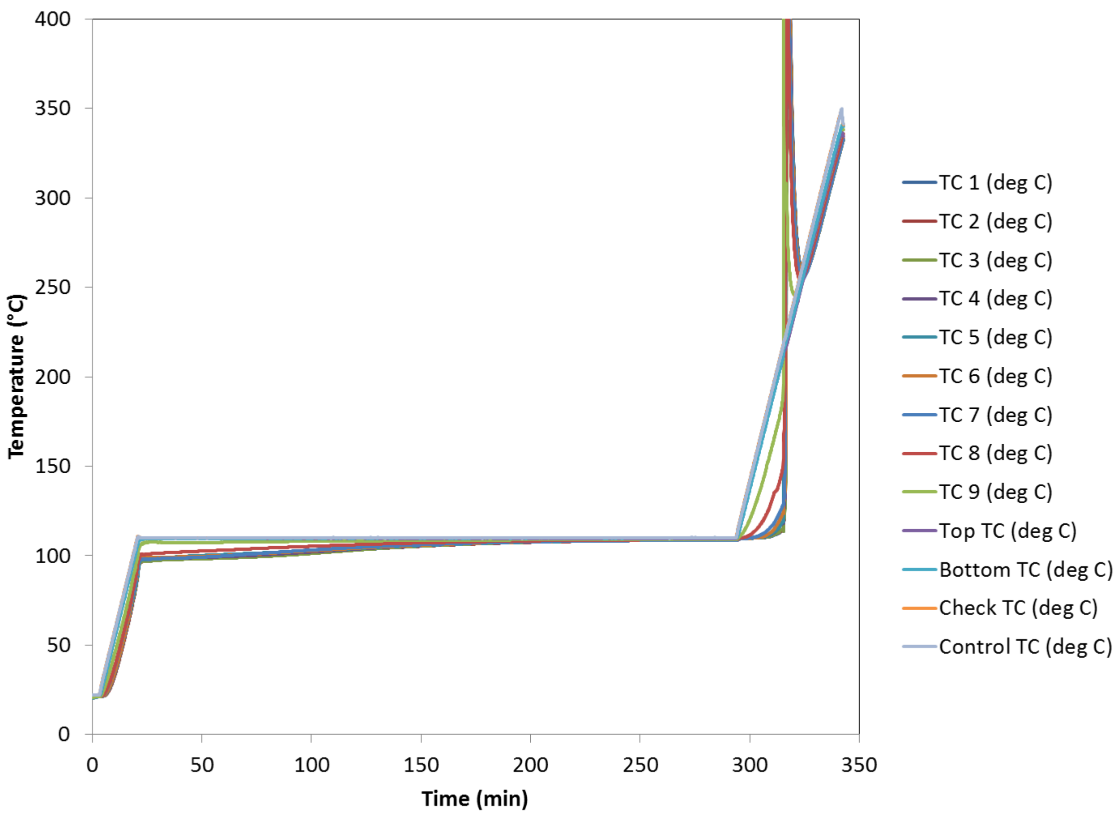


Figure 39. Temperature data from Exp402.

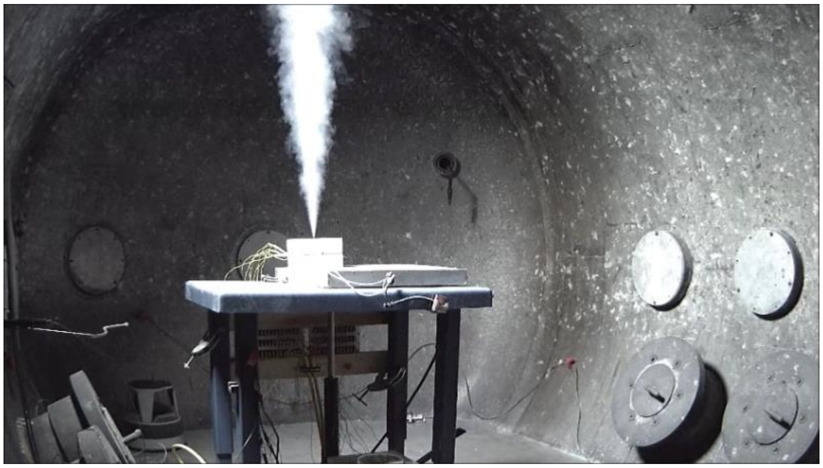


Figure 40. Image from video of Exp402.

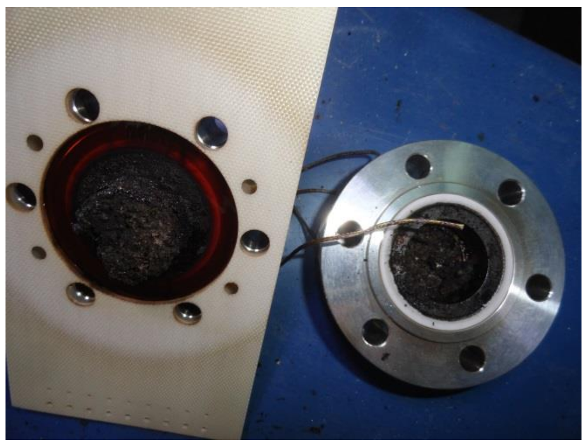


Figure 41. Photo of post-test debris from Exp402.

The results of Exp401 and Exp402 are not conclusive – the lack of exothermic reaction during the long holds at 105°C and 110°C seem to suggest that no runaway reactions occur at these temperatures, but the data do not rule out the possibility that these temperatures did not exceed the boiling point of the liquids present and therefore were regulated by liquid and its vaporization.

<u>Exp403</u>

In December, 2014, the TAT received a report from LANL about TAM (Thermal Activity Monitor) and APTAC (Automatic Pressure Tracking Adiabatic Calorimeter) measurements on certain mixtures of materials believed to be present in Drum 68660. These mixtures contained various ratios of aluminum nitrate nonahydrate, calcium nitrate tetrahydrate, potassium nitrate, chromium nitrate nonahydrate, iron nitrate nonahydrate, water, magnesium nitrate hexahydrate, nitric acid, sodium nitrate, sodium fluoride, nickel nitrate hexahydrate, lead nitrate, oxalic acid, and Swheat. They did not contain Kolorsafe. The results showed exothermic activity in APTAC starting at 55°C in mixtures composed principally of magnesium nitrate hexahydrate, Swheat, sodium nitrate, calcium nitrate tetrahydrate, and iron nitrate nonahydrate. It was found that removing iron nitrate nonahydrate effectively stopped the exothermic activity altogether, demonstrating the likely important role of iron nitrate nonahydrate. Although these experiments did not explore the effects of TEA/TEAN from Kolorsafe, they demonstrated that low temperature reactions occur in mixtures of dry constituents alone.

Based on these results, Exp403 was run with a dry version of the LANL WB-4 mixture, the details of which are listed in Table 3. Table 3 lists the mass percentages for the original WB-4 mixture and the version used in Exp403. For Exp403, the 0.2% water was omitted and the Swheat to salt ratio was adjusted to approximately 1.26:1 by volume. The density of Swheat was assumed to be 0.55 g/cc and that of the salt mixture was assumed to be 1.0 g/cc. The mass percentages calculated from measured masses are listed in Appendix A. The most notable difference between the mixture used in Exp403 and WB-4 is the Swheat to salt ratio.

Table 3. LANL WB-4 mixture and Exp403 target mass percentages.

Substance	LANL WB-4	Exp403
$Ca(NO_3)_2*4H_2O$	8.4	6.63
$Cr(NO_3)_3*9H_2O$	0.1	0.079
$Fe(NO_3)_3*9H_2O$	5.7	4.50
$Mg(NO_3)_2*6H_2O$	20.6	16.3
$NaNO_3$	36.7	29.0
$Pb(NO_3)_2$	1.9	1.50
$(COOH)_2$	1.4	1.11
H_2O	0.2	
Swheat	25	40.9

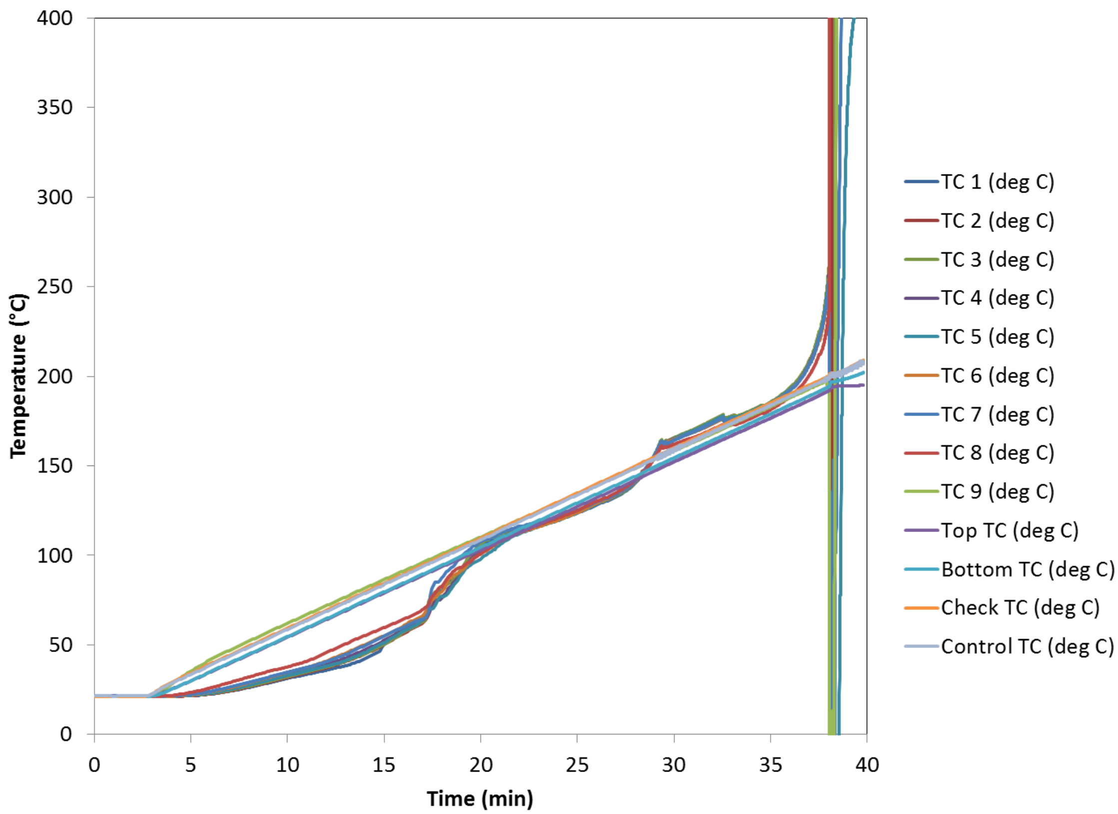


Figure 42. Temperature data from Exp403. Contents were based on the LANL WB-4 mix: Ca nitrate, Cr nitrate, Fe nitrate, Mg nitrate, Na nitrate, Pb nitrate, oxalic acid, and Swheat. No liquids were added.

LANL reported that the WB-4 mixture exhibited exothermic activity starting at 55°C and 100°C in APTAC. Figure 42 shows the start of an exothermic event around 55°C, as the difference between the internal and external temperatures drops to zero. The exothermic activity varies but continues until thermal runaway begins around 190°C.

Ignition in Exp403 was more violent than any previous tests. Figure 43 shows the top insulation block being blown off the assembly. Figure 44 shows that the O-ring failed allowing gases to escape, but that material was also ejected through the top vent.

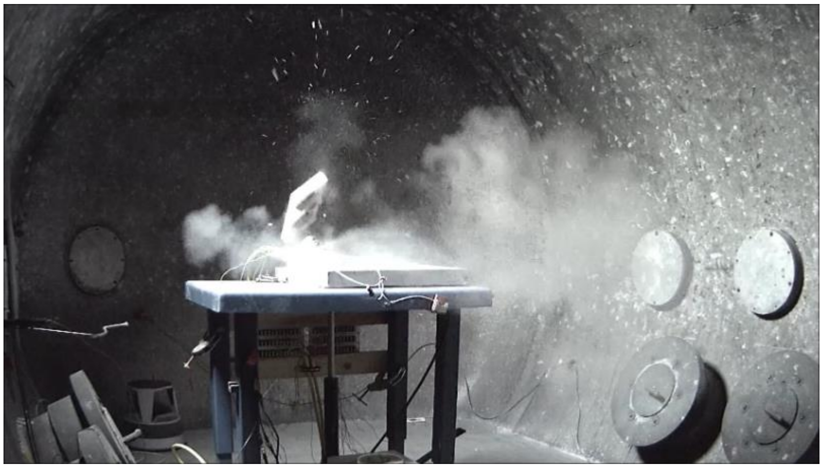


Figure 43. Image from video of Exp403.

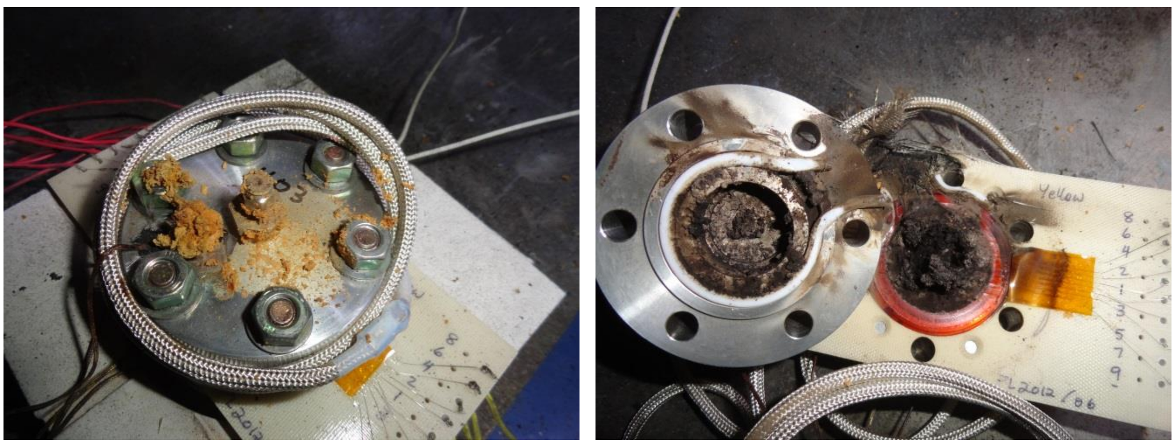


Figure 44. Post-test images from Exp403. The left images shows that a substantial amount of material was expelled through the vent. The right image shows that the O-ring failed.

<u>Exp404</u>

Exp404 was identical to Exp403 except that it contained no Pb and Cr. The quantities of the other salts were adjusted to keep the mass ratios the same. The results were basically the same, indicating that Pb and Cr are not critical to the observed exothermic reactions leading to ignition. In fact, Figure 45 shows that the internal temperatures in Exp404 exceeded the boundary temperature more than in Exp403. The violence of Exp404 was significantly less than in Exp403, so the Pb and/or Cr may have contributed to post-ignition burn rates.

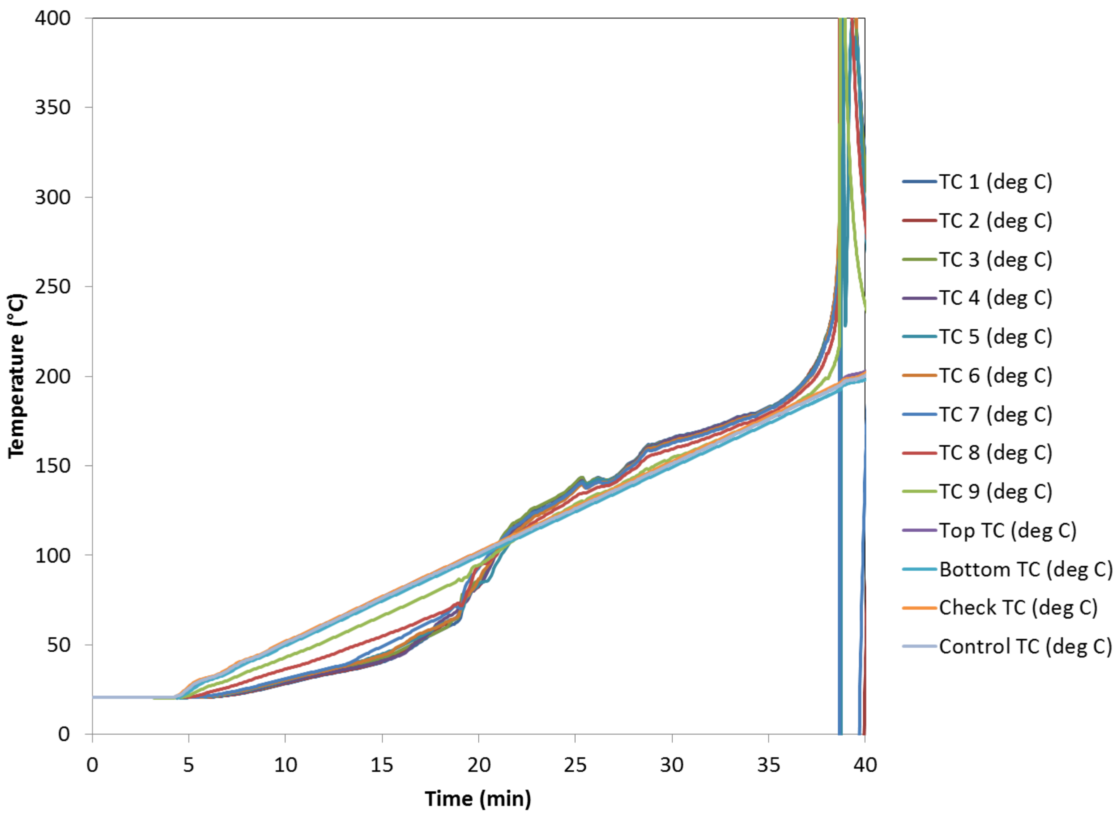


Figure 45. Thermal data from Exp404. Contents were based on the LANL WB-4 mixture and the same as Exp403, but without Pb or Cr.

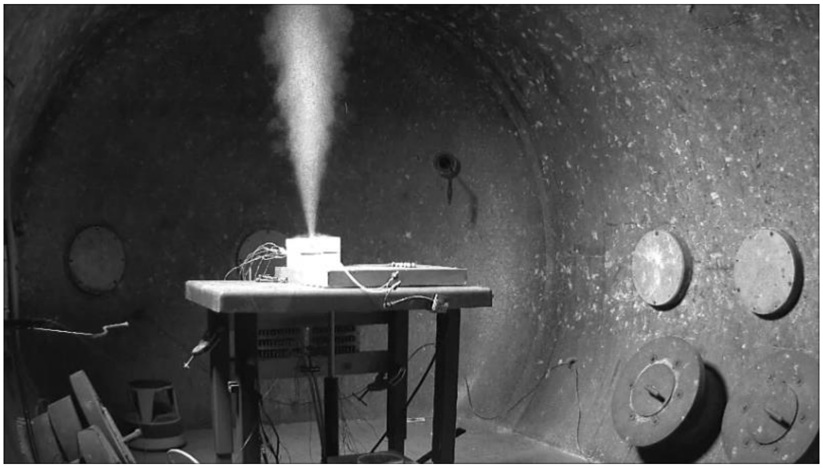


Figure 46. Still image from video of Exp404 showing plume immediately after ignition.

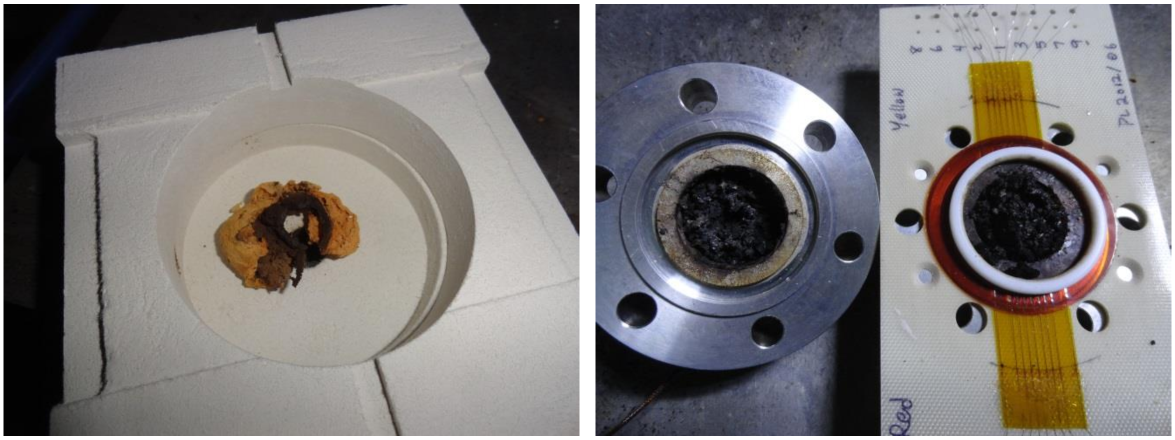


Figure 47. Post-test debris from Exp404. The left image shows material expelled through the vent before ignition, with the appearance of having been molten when ejected.

Exp405

Exp405 was an open test with the LANL WB4 mixture without Pb or Cr. The intention was to observe ignition and determine at what temperature the material ignites when open. The boundary temperature was ramped to 350°C and the material temperature reached about 290°C, without ignition.

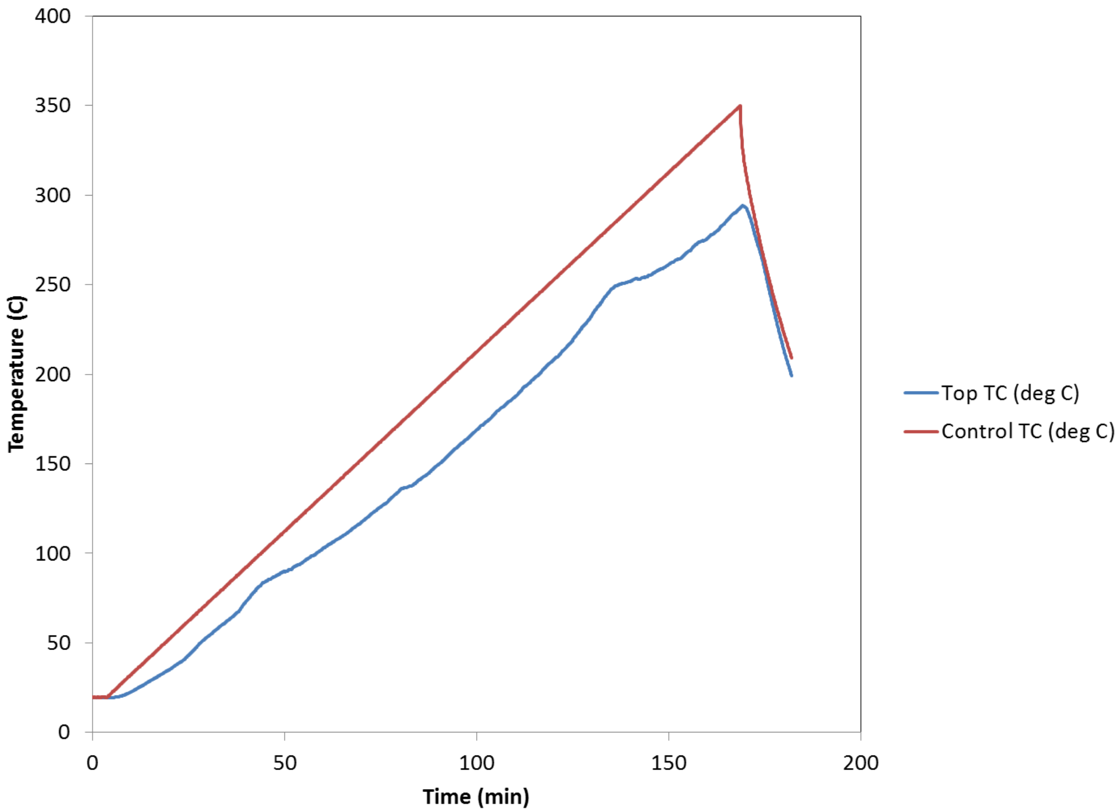


Figure 48. Temperature data from Exp405. The contents were the same as Exp404 (LANL WB-4 mixture without Pb or Cr) and the test was open.

The material expanded substantially, even though no free liquids were present to be absorbed by the Swheat.

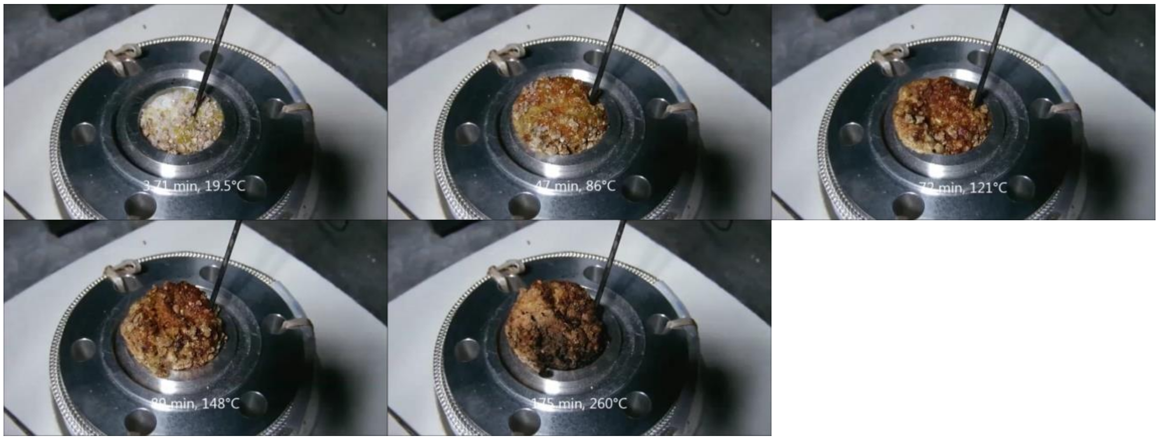


Figure 49. Images from video of Exp405 showing discoloration and expansion.

<u>Exp406</u>

Exp406 used the LANL WB4 mixture without Pb, Cr, or $(COOH)_2$. In addition to evaluating the effect of oxalic acid, a glow plug was set up to attempt to ignite the exhaust plume. The temperature data shown in Figure 50 are very similar to Exp403, which used the entire WB4 mixture, indicating that oxalic acid is not important to the exothermic reactions leading to ignition.

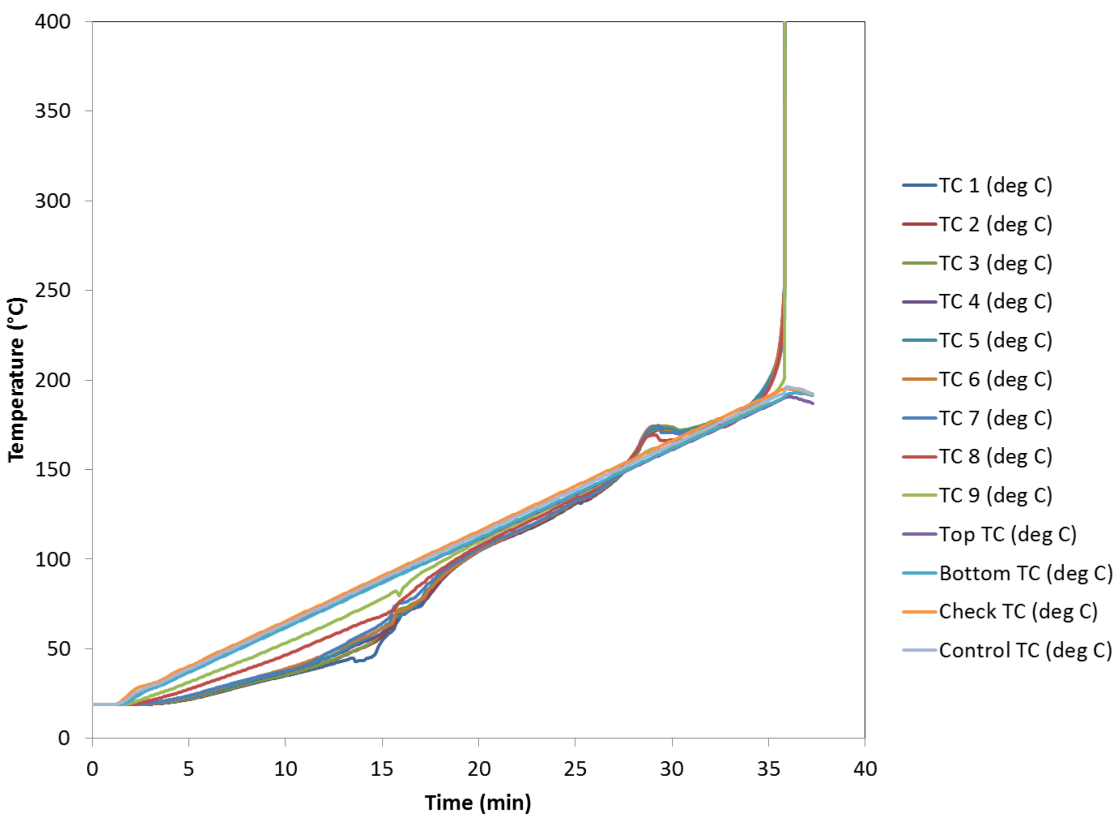


Figure 50. Temperature data from Exp406. Contents were based on the LANL WB-4 mix, without Pb, Cr, or oxalic acid.

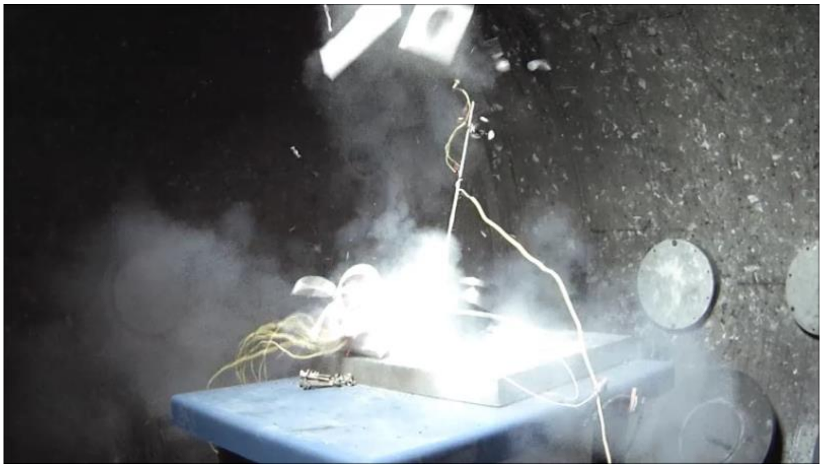


Figure 51. Image from video of Exp406 at ignition.

Exp406 was especially violent. Figure 51 shows the insulation stack being blown apart by the ignition event. Figure 52 shows that the O-ring failed. The exhaust gases were not ignited by the glow plug.

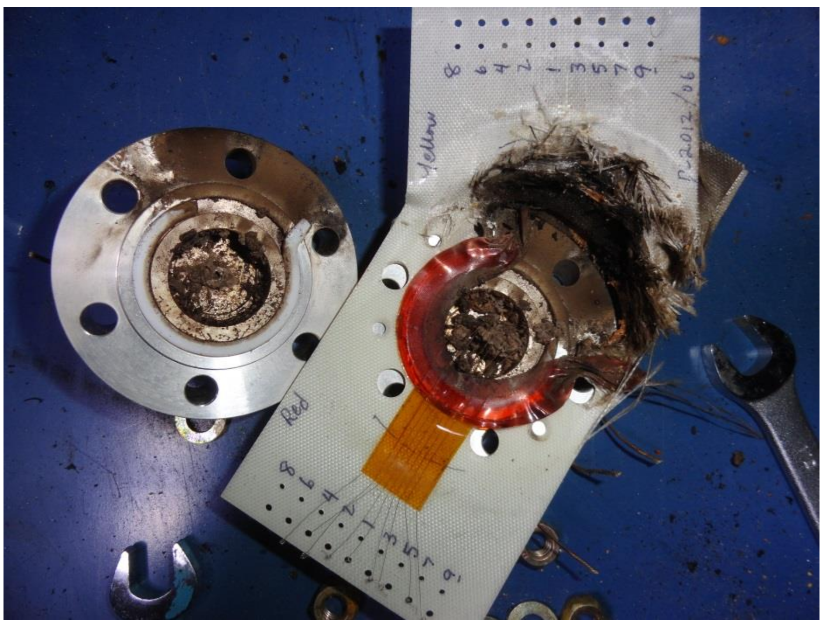


Figure 52. Post-test debris from Exp406.

Exp407

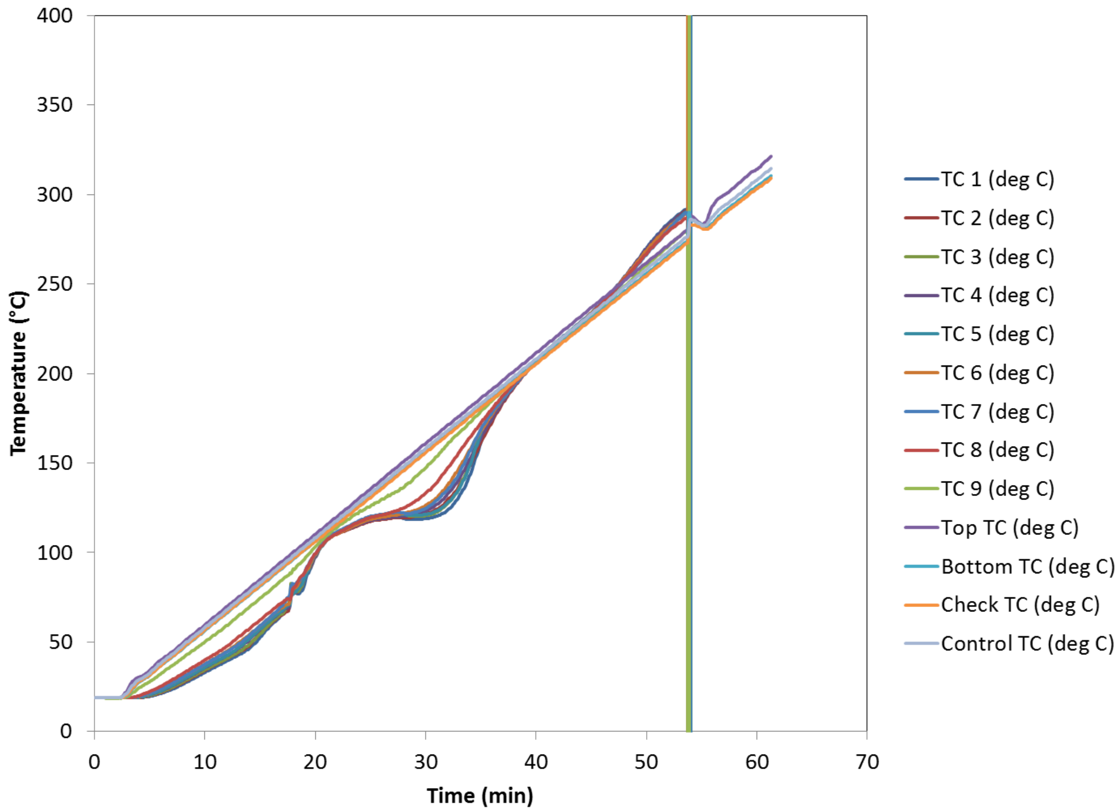


Figure 53. Temperature data from Exp407. Contents were based on the LANL WB-4 mixture, but without Pb nitrate, Cr nitrate, Ca nitrate, or oxalic acid.

Exp407 was based on the LANL WB-4 mixture but without Pb, Cr, oxalic acid, or Ca nitrate. It was the same as Exp406, except without Ca nitrate. A eutectic between Ca nitrate and Mg nitrate is known, and Exp407 was intended to investigate the effect of this eutectic by removing one of the constituents. In comparison with Exp403 (WB-4), Exp404 (WB-4 without Pb or Cr), and Exp406 (WB-4 without Pb, Cr, or oxalic acid), Figure 53 shows similar exothermic behavior up to about 100°C, but in contrast the exothermic reactions then stop. Self-heating returns between about 150°C and 200°C, leading to ignition around 275°C. This was much higher temperature than the previous tests, confirming the importance of Ca nitrate.

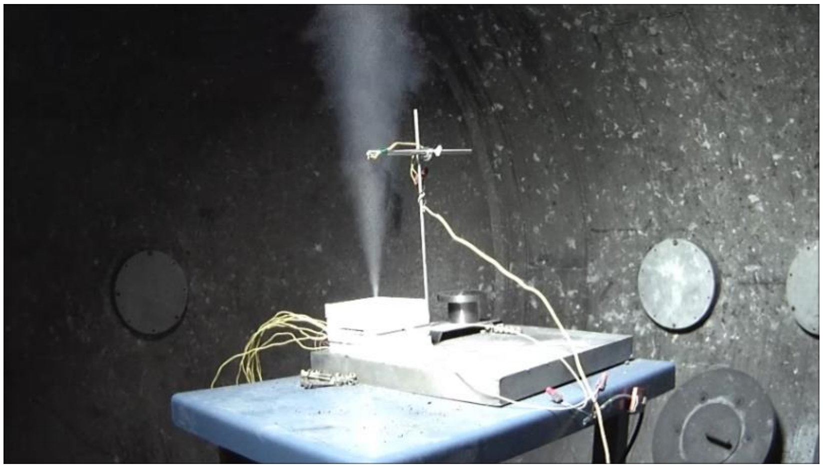


Figure 54. Image from video of Exp407, at ignition.

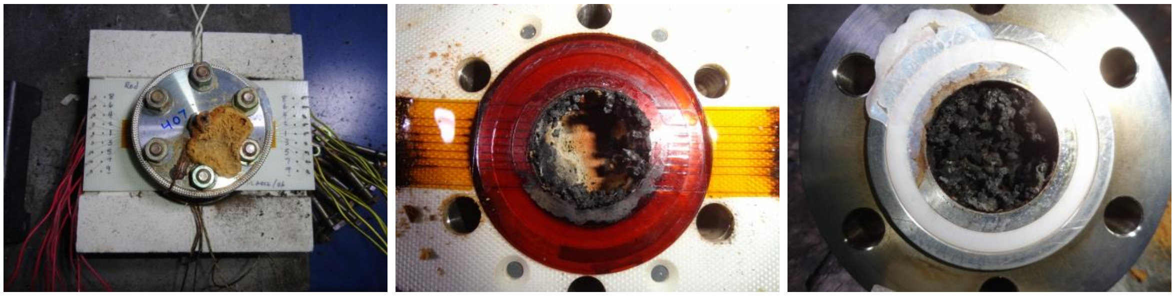


Figure 55. Post-test pictures from Exp407.

Exp407 was not particularly violent. Ignition resulted in a plume, as seen in Figure 54, but the O-ring remained intact as seen in Figure 55. Again, the plume did not ignite.

<u>Exp408</u>

Exp408 used a mixture based on the WB-4 mix, but without Fe nitrate. LANL reported that a similar mixture did not exhibit exothermic behavior. Figure 56 shows that the exothermic activity seen in similar tests between about 60°C and 100°C is not present, although exothermic activity does appear to be present starting around 100°C. A sudden drop in the internal temperatures around 38 minutes (200°C) was associated with a sudden release in the video, indicating that the vent had become blocked and this blockage suddenly failed. The activity prior to this was presumably dependent on the vent being blocked, and similar behavior may have occurred in other tests. Ignition occurred at about 260°C, significantly higher than in Exp403, Exp404, or Exp406, indicating that Fe nitrate plays a significant role in ignition behavior.

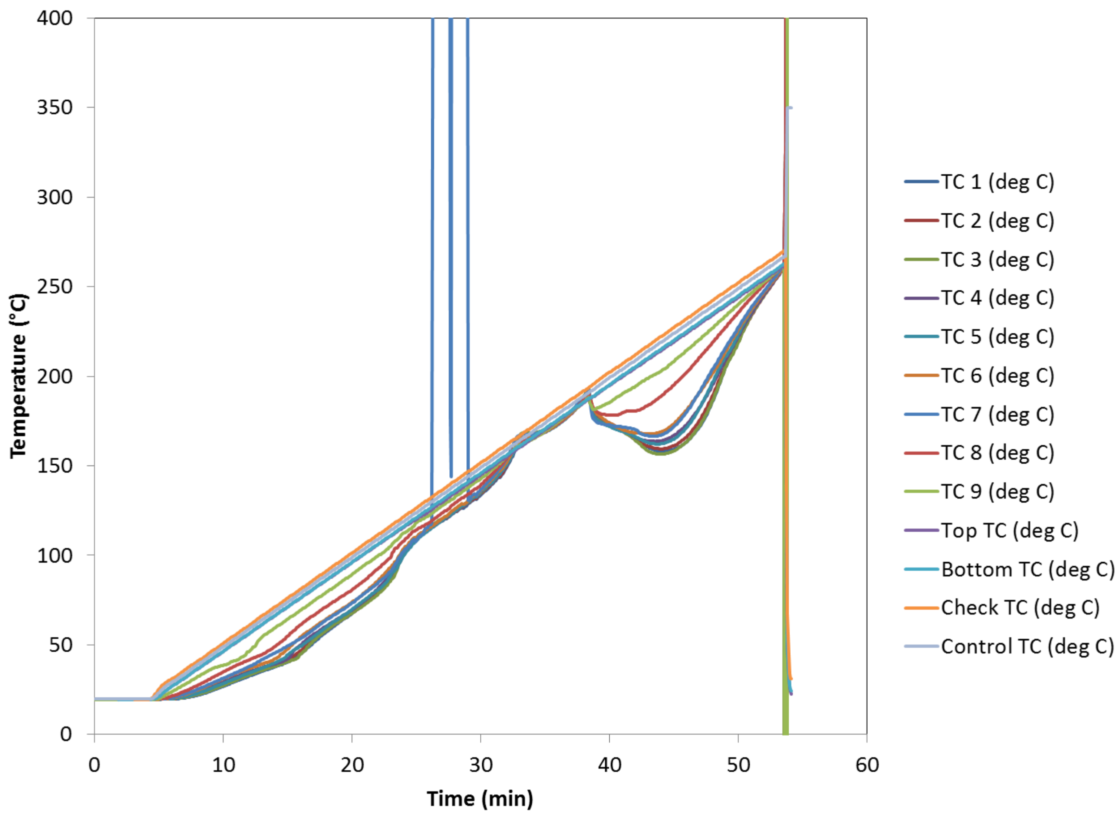


Figure 56. Temperature data from Exp408. Contents were based on the LANL WB-4 mixture, but without Fe nitrate.

Figure 57. Image from video of Exp408 showing explosion.

Exp408 was relatively violent, as shown by Figure 57. The video showed smoke venting from the vessel before ignition, indicating that the vent was not clogged. Again, the plume did not ignite. The violence is also apparent in Figure 58, which shows that the O-rings were ejected, the thermocouple board was split in half, and soot was deposited on the flanges. Very little material was left inside the vessel, but the bolts did not break.

Figure 58. Post-test debris from Exp408.

<u>Exp409</u>

Exp409 used the LANL SA mix without liquid. Previous tests with the LANL SA mix had involved liquid, and recent tests with different versions of the LANL WB-4 mix had been conducted without liquid. Exp409 sought to determine if the different behavior was a result of the liquid or the salt mixture.

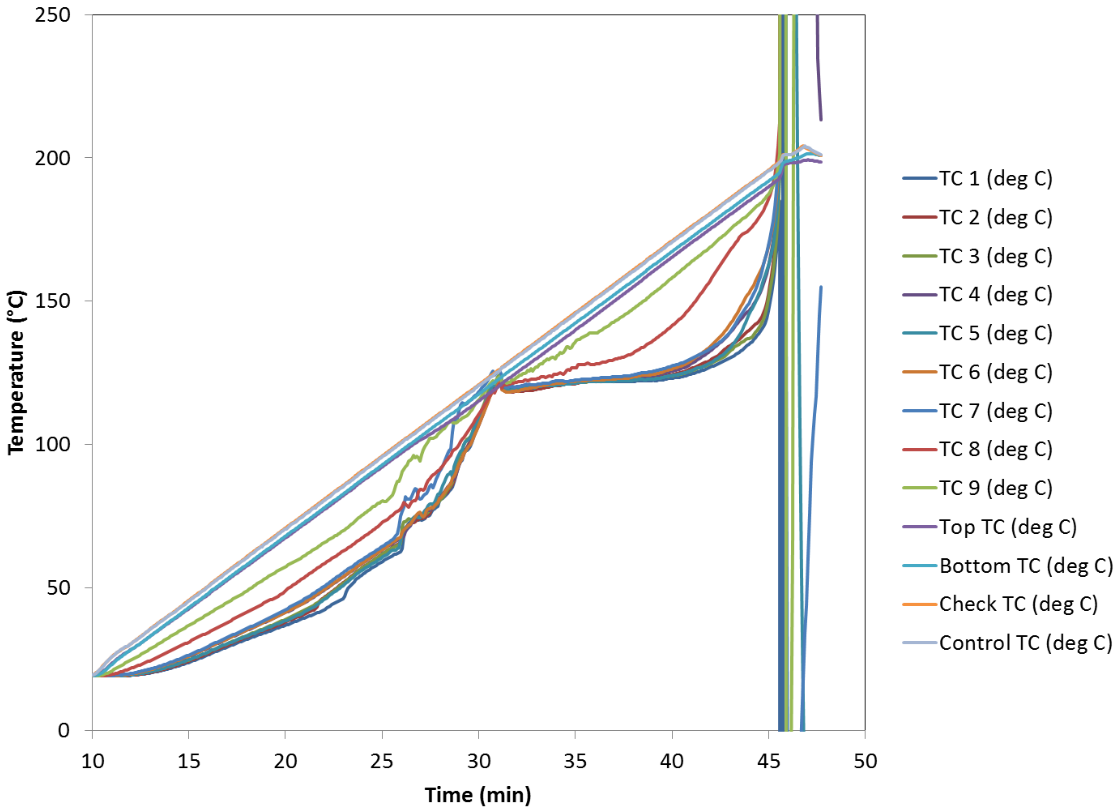


Figure 59. Temperature data from Exp409. Contents were the LANL SA mix and Swheat.

The comparable experiment with the LANL SA mix and over-neutralized nitric acid was Exp398. Unfortunately most of the thermocouples in Exp398 failed early, but some observations can be made by comparing Figure 59 and Figure 30. Exp398 was apparently dominated by vaporization of water occurring just above 100°C. A similar effect is visible in Exp409, but occurring at a somewhat higher temperature of about 120°C. Since no liquid was added to Exp409, this vaporization is apparently a result of water evolved from hydrates. Ignition in

Exp398 occurred when the outer temperatures were about 236°C while in Exp409 the outer temperatures were about 190°C. In both cases ignition apparently occurred quickly once the water was completely vaporized, and since less water was present in Exp409, this happened sooner.

The comparable experiment with the LANL WB-4 mixture without liquid was Exp403. The most notable difference is the water vaporization in Exp409, which is not apparent in Exp403. This is perhaps related to the greater quantity of hydrates (notably Mg nitrate hexahydrate) in Exp409 vs. Exp403. Ignition in the two tests happened at around the same outside temperature.

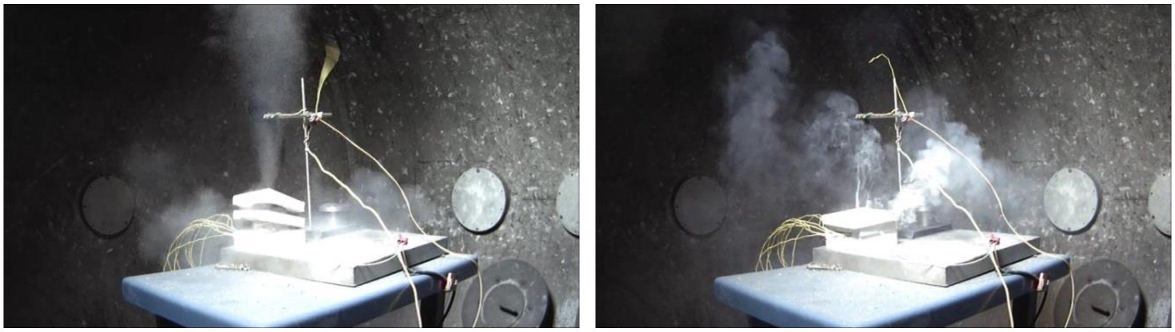


Figure 60. Images from video of Exp409. The left image shows a jet and the insulation stack being blown apart at ignition. The right image shows the remains of the experiment continuing to exhaust smoke.

Figure 60 shows images from the video. Smoke was observed venting from the experiment prior to ignition, indicating that the vent was not clogged. A spark gap positioned in the plume area was fired several times during the test to try to ignite the exhaust gases, but no ignition was observed.

Figure 61. Post-test debris from Exp409.

The left image in Figure 61 shows yellow-ish red residue on the vessel, outside the exhaust vent. The other images show a significant amount of char left inside the vessel.

Exp410 and Exp411

Exp410 and Exp411 were run with the LANL WB-4 mixture without water, Pb, or Cr, at 2°C/min and 1°C/min, respectively. The objective was to compare with Exp404, which used the same mixture but was run at 5°C/min. Comparing Figure 62 with Figure 45, for the most part the same features appear, but are more distinct in Exp410. In both cases the internal temperatures rise suddenly when they reach 65-69°C and subsequently rise above the external temperatures. This is likely due to formation of a eutectic, which may both increase the heat transfer rate (causing the temperature gradient to drop) and increase reaction rates. In both cases the internal temperatures increase faster than the external temperatures, indicating the occurrence of an exothermic process, but then slow down prior to the onset of thermal runaway. In Exp404, the thermal runaway appears to start around 180°C and in Exp410 it appears to start around 163°C, and ignition occurs in Exp404 when the boundary temperatures are about 195°C and in Exp410 when the boundary temperatures are about 178°C. This relationship is typical and expected for reaction rates that depend on extent of reaction as well as temperature.

A spark gap was positioned above the experiment, where the exhaust plume was expected to flow, and triggered a number of times during the experiment both before and after ignition. The right image in Figure 63 shows the spark gap firing. In no case was combustion of the exhaust observed. The video did not clearly show gases venting from the vessel prior to ignition, so the vent may have been clogged.

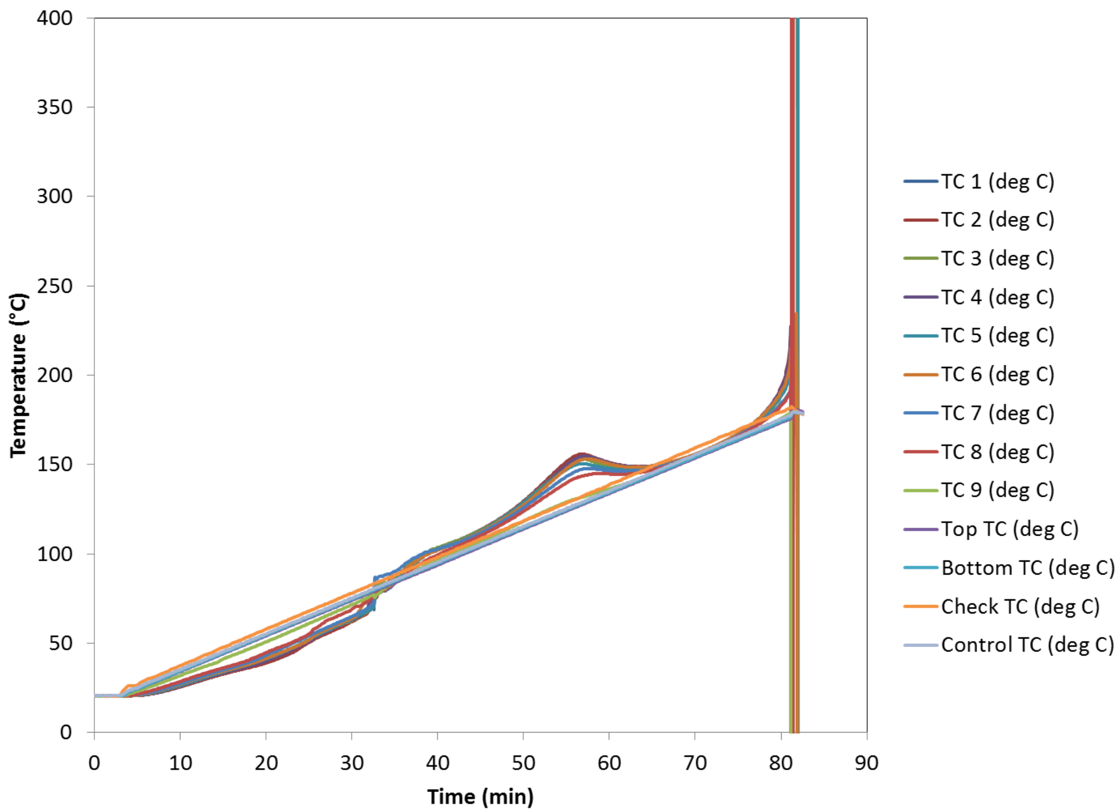


Figure 62. Temperature data from Exp410. Contents were the LANL WB-4 mix without water, Pb, or Cr. Heating rate was 2°C/min.

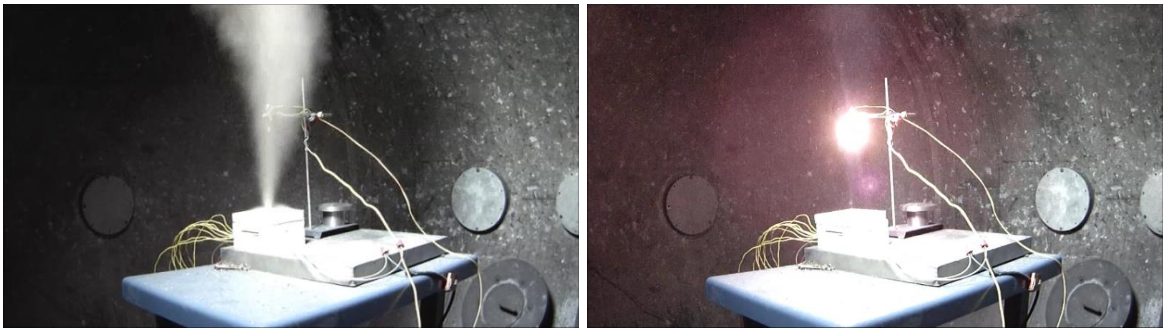


Figure 63. Images from video of Exp410. The left image was taken immediately after ignition, and the right shows the spark gap discharging.

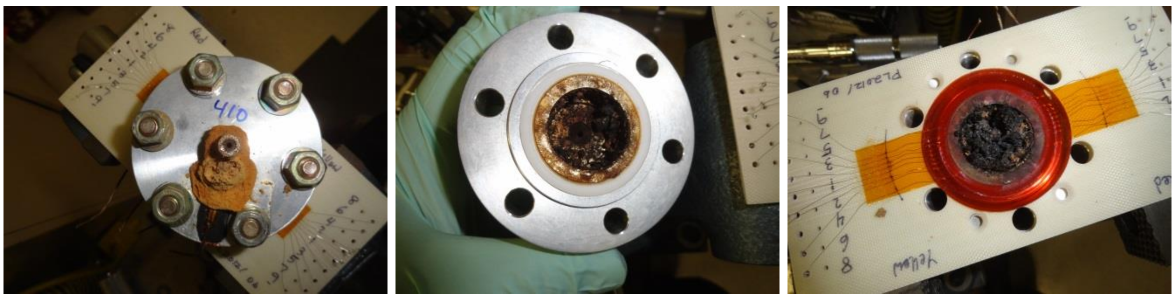


Figure 64. Post-test debris from Exp410.

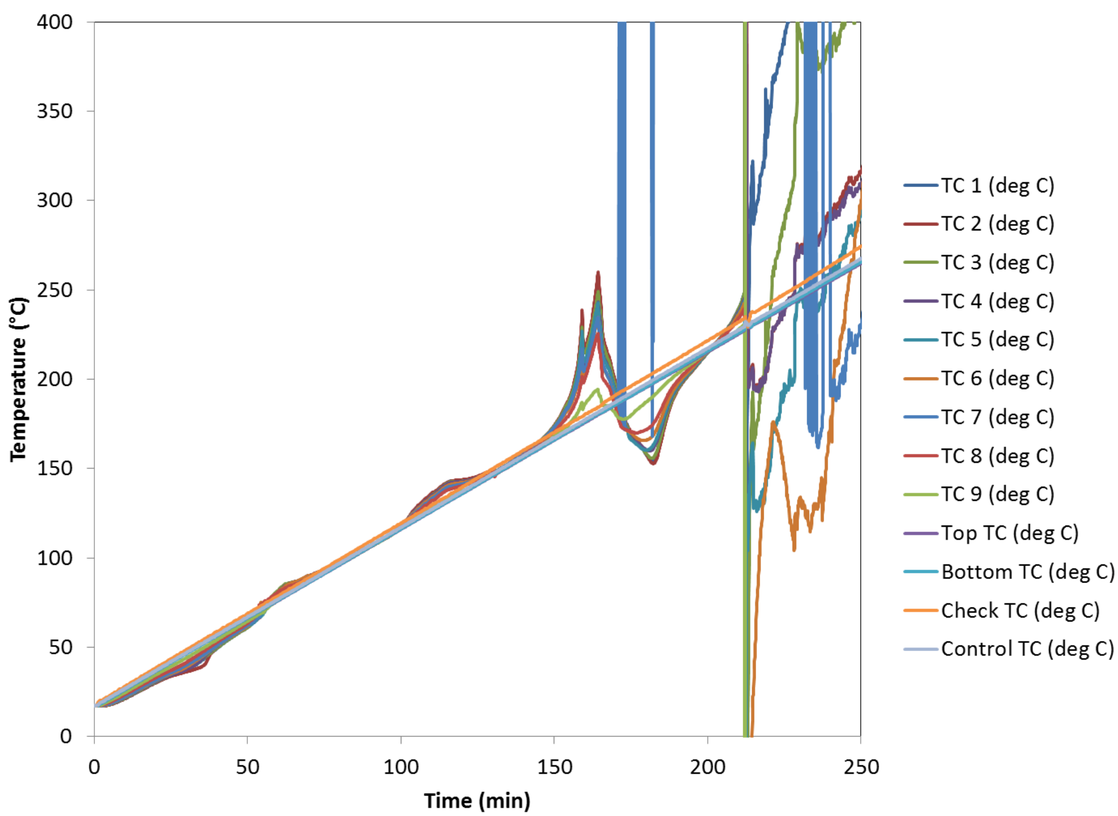


Figure 65. Temperature data from Exp411. Contents were the LANL WB-4 mix without water, Pb, or Cr. Heating rate was 1°C/min.

Figure 66 shows a comparison of Exp404, Exp410, and Exp411. The center and control temperatures are plotted. The low temperature exotherm occurs at lower temperatures with slower ramp rate, as expected. As indicated by the center temperature crossing the control temperature, the start of the exotherm occurs at 105.7°C, 86.6°C, and 54.8°C at 5°C/min, 2°C/min, and 1°C/min, respectively. This trend is expected to continue at lower heating rates, possibly to ambient temperature.

At higher temperatures, the differences are not as regular. A peak in temperature occurs around 150°C in all cases. A final exotherm begins around 175°C and 160°C in the higher heating rate cases, but the corresponding exotherm does not lead to final ignition at 1°C/min. Instead, at the lowest heating rate this exotherm is followed by a deep endotherm and finally ignition. This endotherm appears to be caused by vaporization of water evolved from decomposition of hydrates, suggesting that this step was suppressed or overwhelmed by higher exothermic rates at the higher heating rates.

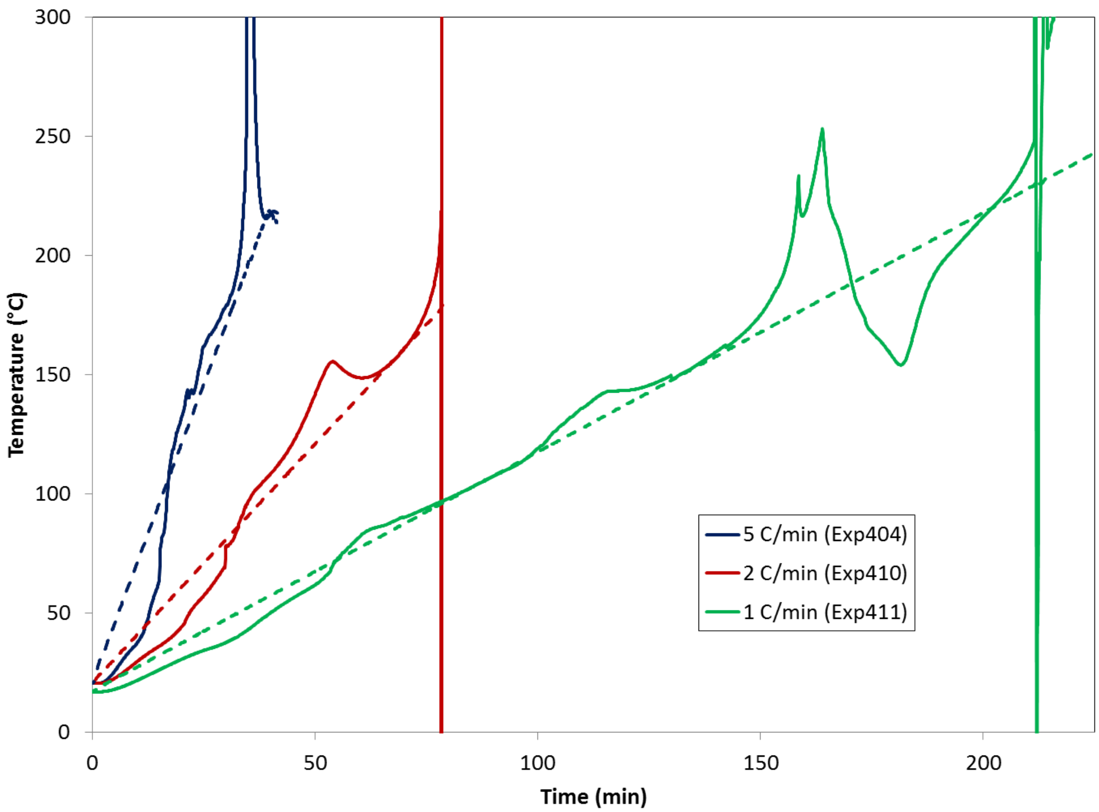


Figure 66. Comparison of Exp404, Exp410, and Exp411 - WB-4 mixture without Pb, Cr, or water run at 5°C/min, 2°C/min, and 1°C/min.

3. Results - Thermal Properties

Thermal properties were determined from the SITI thermocouple data following the procedure defined in ref. 1. This analysis computes thermal diffusivity directly from temperature

[1] W.W. Erikson, M.A. Cooper, M.L. Hobs, M.J. Kaneshige, M.S. Oliver, and S. Snedigar, "Determination of thermal diffusivity, conductivity, and energy release from the internal temperature profiles of energetic materials," International Journal of Heat and Mass Transfer (79), pages 676-688.

measurements during a ramp, in the absence of exothermic or endothermic events. Thermal conductivity can be calculated from thermal diffusivity if specific heat and density are known. In general, specific heat is not known for the mixtures of interest. Estimating it is possible but has not been done.

Figure 67 shows thermal diffusivity estimated from the thermocouple data from Exp387, Exp388, and Exp389, all tests with Swheat and liquid but no nitrate salts. All of the data up to 90°C are shown, even though not all are valid, in order to illustrate the limits of validity. The analysis assumes a steady ramp with no transient effects due to changing heating rates, and therefore the initial data, which are affected by the start-up transient, are not valid. This is true up to about 30°C. In the case of Exp387, the temperatures rose to about 95°C and then stopped rising due to the vaporization of water, and also exhibited upward curvature just before the vaporization, effectively ending the validity of the data at about 90°C, which is also where the apparent diffusivity peaks and suddenly drops. These results show increasing diffusivity with temperature.

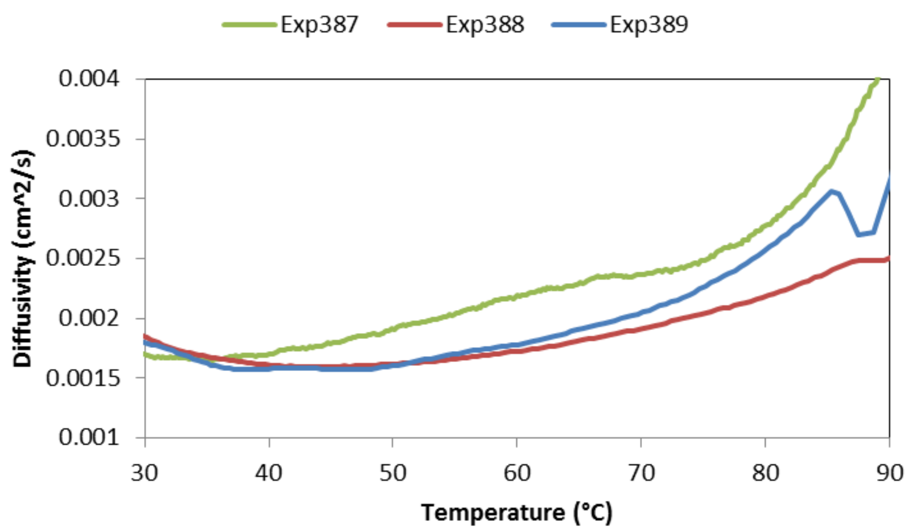


Figure 67. Thermal diffusivity estimated from the Exp387, Exp388, and Exp389 thermocouple data.

Figure 67 shows the estimated thermal diffusivity from Exp388 over the valid range. In this case, the lower limit is higher than for Exp387 because the heating rate was higher (5°C/min vs. 2°C/min).

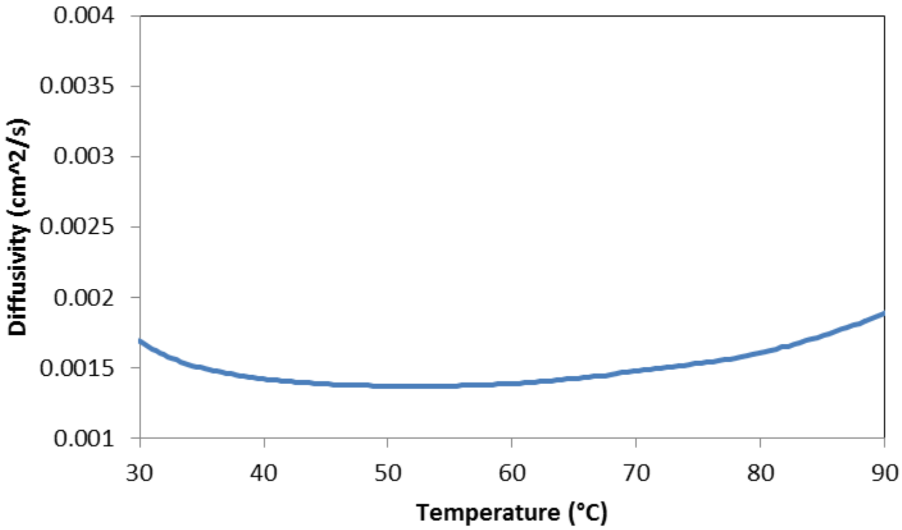


Figure 68. Thermal diffusivity estimated from Exp390.

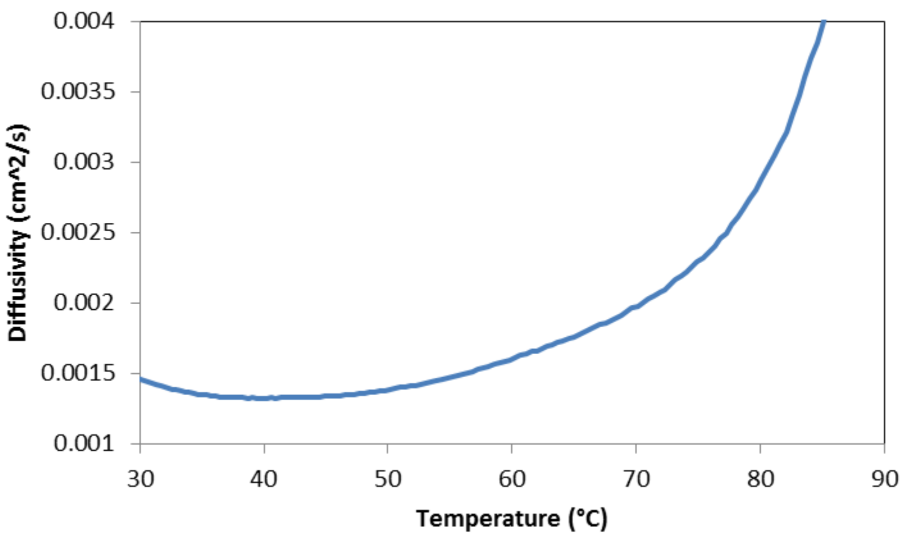


Figure 69. Thermal diffusivity estimated from Exp392.

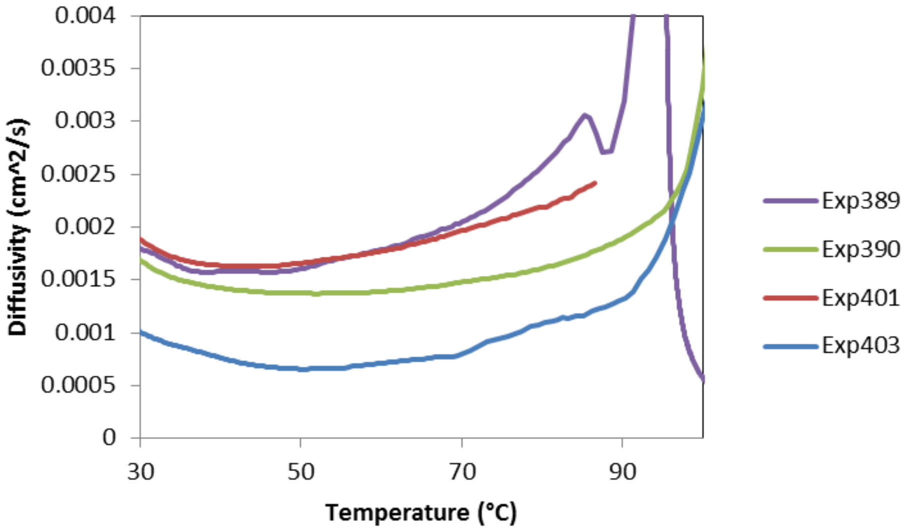


Figure 70. Comparison of thermal diffusivity calculated for different mixtures. Exp389 was Swheat and water. Exp390 was Swheat, Na and Mg salts, and neutralized acid. Exp401 was the LANL Stream Analyzer mix, Swheat, and over-neutralized acid. Exp403 was the LANL WB-4 mix without water and Swheat.

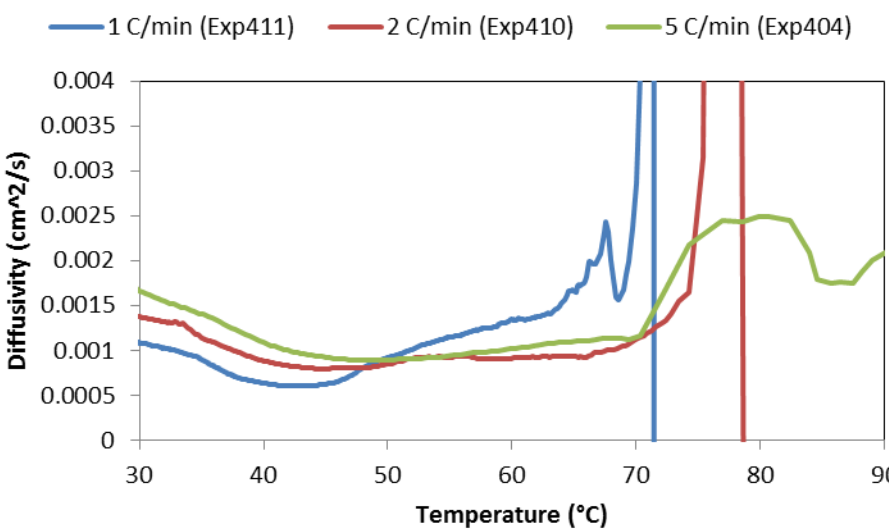


Figure 71. Estimated thermal diffusivity from three different heating rates.

4. Supporting Data

The densities of the remediated salt and liquid layers as determined in the thermal modeling section were 738 and 848 kg/m3, respectively. The specific heat was also assumed to be 2400 J/kgK. The thermal conductivies of the remediated salt and liquid layers using a thermal diffusivity of 0.0015 cm^2/s are 0.3 and 0.4 W/mK, respectively. These thermal conductivities were used in the thermal modeling section.

5. Potential Additional Work

Following are some areas where additional work could substantially improve upon the results presented here.

1. Use salts soaked in acid, or add acid to the dry mixes.
2. Dry wet mixtures to compare mixtures with and without TEAN.
3. Test the effect of glove material.
4. Gas sampling/analysis
5. Measure heat capacity to determine thermal conductivity from measured diffusivity.
6. Ignition experiments with gases produced after the moisture has been removed.

Appendix A – Composition of tested mixtures.

Table 4. Nominal Compositions, by mass (mg) except where noted.

Test	Liquid	Solid Mass (g)	Swheat	Al Nitrate	Ca Nitrate	K Nitrate	Cr Nitrate	Fe Nitrate	Na Nitrate	Mg Nitrate	NaF	Ni Nitrate	Pb Nitrate	Oxalic Acid
Exp386	4.7 ml tap water	5170	5170											
Exp387	4.7 ml DI water	5170	5170											
Exp388	4.7 ml NNA	5170	5170											
Exp389	4.7 ml DI water	5170	5170											
Exp390	4.7 ml NNA	6.86	4820						528	1507				
Exp391	1.37 ml UNNA	1.00	500						130	370				
Exp392	2.75 ml UNNA	6.86	4820						528	1507				
Exp394	2.75 ml ONNA	10.1	4820						1367	3900				
Exp395	2.75 ml ONNA	10.1	4820						1367	3900				
Exp396	2.75 ml ONNA	6.86	4820						528	1507				
Exp397	1.37 ml ONNA		2410	25	98	21	1.3	67	142	645	2	0.7	0.1	16
Exp398	2.75 ml ONNA	6.85	4820	49	196	43	2.6	134	283	1290	3.8	1.3	0.2	32
Exp399	2.61 ml ONNA	6.86	4820						528	1507				
Exp400	N/A (ignition test with remains of Exp397)													
Exp401	2.75 ml ONNA	6.86	4820	49	196	43	2.6	134	293	1290	3.8	1.3	0.2	32
Exp402	2.75 ml ONNA	6.86	4820	49	196	43	2.6	134	293	1290	3.8	1.3	0.2	32
Exp403	None	10.6	4324		701		8.34	476	3060	1720			159	117
Exp404	None	10.6	4324		720			489	3146	1766				120
Exp405	None	5.28	2162		360			245	1573	883				60
Exp406	None	10.6	4324		732			498	3207	1800				
Exp407	None	10.6	4324					564	3635	2040				
Exp408	None	10.6	4324		759		9		3314	1860			172	126
Exp409	None	10.6	4324	151	601	132	8	410	868	3957	12	4	0.6	97
Exp410	None	10.6	4324		720			489	3146	1766				120
Exp411	None	10.6	4324		720			489	3146	1766				120

Table 5. Actual compositions. Solids are listed as mass percentages of the solids. Liquids are listed separately.

Test	Liquid	Solid Mass (g)	Swheat	Al Nitrate	Ca Nitrate	K Nitrate	Cr Nitrate	Fe Nitrate	Na Nitrate	Mg Nitrate	NaF	Ni Nitrate	Pb Nitrate	Oxalic Acid
Exp386	4.71 g tap water	5.17	100											
Exp387	4.7 g DI water	5.17	100											
Exp388	4.7 g NNA	5.17	100											
Exp389	4.7 g DI water	5.17	100											
Exp390	2.7 ml NNA	6.86	70.3						7.70	22.0				
Exp391	1.37 ml UNNA	1.02	50.7						13.0	36.3				
Exp392	2.75 ml UNNA	6.85	70.3						7.71	22.0				
Exp394	2.75 ml ONNA	10.1	47.8						13.5	38.7				
Exp395	2.75 ml ONNA	10.1	47.6						13.5	38.9				
Exp396	2.75 ml ONNA	6.84	70.4						7.61	22.0				
Exp397	1.37 ml ONNA	3.40	70.4	0.574	9.28	0.671	0.0147	1.89	4.15	19.1	0.0707	0.053	0.0147	0.389
Exp398	2.75 ml ONNA	6.86	70.6	0.653	2.77	0.672	0.0306	2.31	4.03	18.4	0.0845	0.0233	0.0146	0.488
Exp399	2.61 ml ONNA	6.85	70.4						7.62	22.0				
Exp401	2.75 ml ONNA	6.82	70.8	0.722	2.87	0.629	0.0352	1.97	4.06	18.3	0.0367	0.0367	7.33e-6	0.487
Exp402	2.75 ml ONNA	6.82	70.9	0.688	2.86	0.654	0.0440	1.94	4.03	18.5	0.0425	0.0161	7.33e-6	0.400
Exp403	None	10.6	41.2		6.80		0.0781	4.51	28.7	16.1			1.48	41.2
Exp404	None	10.6	40.7		6.86			4.56	30.0	16.7				1.14
Exp405	None	5.28	40.9		6.75			4.59	29.5	16.8				1.16
Exp406	None	10.6	40.9		6.91			4.69	30.5	17.0				
Exp407	None	10.6	40.9					5.35	34.4	19.4				
Exp408	None	10.7	40.5		7.13		0.118		31.7	17.7			1.65	1.18
Exp409	None	10.6	40.9	1.44	5.69	1.30	0.0755	3.86	8.27	37.4	0.108	0.0566	0.00472	0.906

Exp410	None	10.5	41.0		6.85			4.60	29.7	16.6				1.18
Exp411	None	10.6	40.9		6.86			4.62	29.7	16.8				1.15

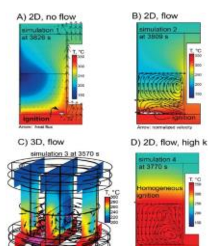
Appendix B – Test Plan

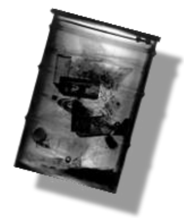
Exceptional service in the national interest

Test Plan

Sandia Instrumented Thermal Ignition (SITI)

14 December 2014





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Sandia Instrumented Thermal Ignition (SITI)

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December 14, 2014

6. Objectives

The Sandia Instrumented Thermal Ignition (SITI) small-scale slow cook-off apparatus will be used to investigate thermal decomposition reactions in mixtures of materials associated with drum 68660 and that are candidates for mid-scale (10 gallon) drum tests or that are outside the scope of the 10-gallon drum tests. Heat release and ignition will be measured as the mixtures are heated to compare reactivity of different mixtures. The different mixtures will represent binary parameter studies (changing one variable at a time to evaluate its effect). The results will also be used to determine thermal properties and to support refinement of hypothetical reaction mechanisms and cook-off ignition models.

7. Sandia Instrumented Thermal Ignition (SITI) experiment

The SITI apparatus, illustrated in **Figure 72**, is typically used to study slow cook-off ignition of energetic materials. As a sample is heated, thermal decomposition reactions generate heat, which is observed with a grid of thermocouples in the middle of the sample, and gases, which are observed as headspace pressure.

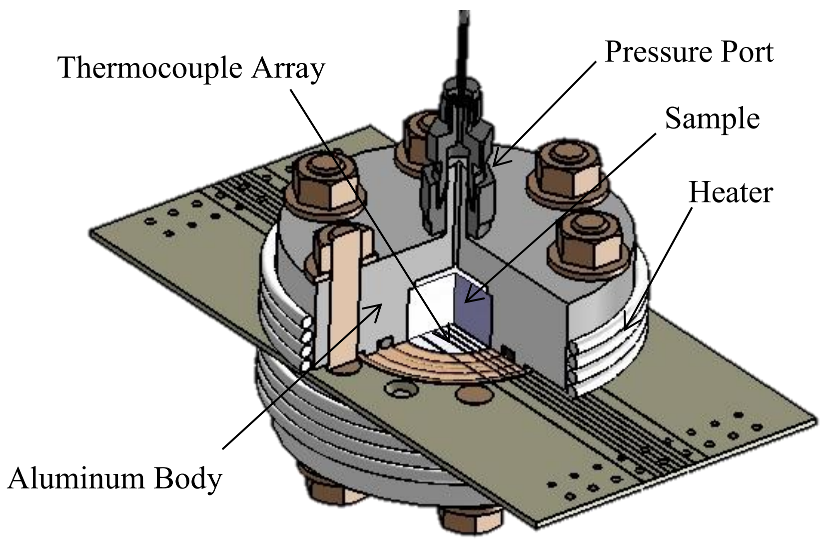

Figure 72. Cutaway illustration of the Sandia Instrumented Thermal Ignition (SITI) experiment. Insulation is not shown.

The specimen is 25.4 mm diameter and 25.4 mm tall, separated into two halves between which the thermocouple grid is placed. Nine thermocouple wires provide spatially resolved temperature measurements from the center to the edge of the specimen. The body is aluminum and the assembly is encased in insulation to approximate an isothermal (uniform) boundary condition on the sample. The thermocouple wires are sealed inside a Kapton gasket and the assembly is sealed gas tight with O-rings, enabling measurement of pressurization. Tests can also be run fully vented.

Heat is provided by a resistive rope heater wrapped around the assembly and controlled by a feedback temperature controller. Typically a material is studied by heating to a number of different set point temperatures and observing thermal decomposition and ignition. Alternatively, the temperature can be ramped continuously from ambient to ignition. A method has been developed to derive thermal properties (specifically thermal diffusivity) from linear ramp data. Other temperature profiles are possible.

8. Test Matrix

The immediate focus of this test plan is to support selection of mixtures for investigation in the mid-scale 10-gallon drum tests, and as such the rationale and process for selection of candidate mixtures is the same. These tests are different from the planned 10-gallon drum tests in the following ways:

- Scale – the 10-gal drum tests will contain about 2000x more material than SITI.
- Temperature – the 10-gal drum tests will be run with ambient initial and boundary temperatures. SITI initial temperature is ambient but the boundary temperature will be ramped until ignition or 350°C, whichever happens first.
- Layering – absorbed liquids and nitrate salts will be in distinct layers in the 10-gal drum tests, but mixed in SITI.

The nominal test protocol and matrix are defined here. Possible variations are described later. **Table 6** shows a matrix of the planned test conditions. Each test is intended to answer a specific question related to the role of a particular constituent or combination of constituents, or provide control for another experiment.

In order to evaluate and compare a number of different mixtures, as opposed to study a particular mixture in detail, each test will consist of a continuous ramp from ambient to 350°C at 5°C/min. This ramp rate results in tests of reasonable duration, which is necessary to accomplish a number of tests in a short period, but will compromise observation of slow reactions, including probably microbiological activity. The primary results of each test will be thermal properties of that mixture, a comparison of endo/exothermic activity observed as a function of temperature relative to other mixtures, and whether or not the material ignites and at what temperature.

General Notes:

1. Tests will not in general be performed in the order listed. Operational constraints and availability of materials will dictate order, but in general the "most interesting" tests will be performed sooner in order to establish "worst case" responses. Subsequent tests will seek to show which aspects were responsible for those responses through elimination.
2. Volume of Swheat will be based on mass using a standardized bulk density of 0.55 g/cc.
3. Neutralized HNO_3 starts with 3.3M HNO_3.
4. Neutralizer is Spilfyter Kolorsafe (KS) Liquid Acid Neutralizer.
5. Underneutralized and overneutralized acid will be used to study the possible effects of adding too little or too much neutralizer during the remediation process. The pH of underneutralized acid is expected to be 0-1 and will address the effect of acidity on reactivity. This may cause difficulties due to reaction with the aluminum vessel. The pH of overneutralized acid is expected to be 7-8. This will address the effect of excess TEA.
6. Swheat to liquid ratio is 2:1 by volume, unless noted.[2]
7. Swheat to salt ratio is 1.26:1 by volume, unless noted.[2]
8. Na and Mg salts are mixed 1:1 by mass of cation (not by total hydrated salt mass).
9. Pb nitrate will be added as 0.1% of the mass of Na, by mass of cation.
10. The LANL Stream Analyzer-predicted salt composition is listed in **Table 7.** LANL has stated that experiments with this mixture were more reactive than others. Based on consultation with LANL, this composition will be simplified for use.
11. Solid materials will be loaded into the experiment first. Liquids will be injected through the gas port on the top after assembly.
12. Tests will be run vented, initially, to best replicate the expected conditions inside a TRU waste drum, which is vented. No measurement of gas generation is available when the experiment is vented, so tests may also be run sealed with measurement of pressure as an indication of gas generation.

[2] The rationale for Swheat ratios are described in a separate document "Swheat Ratios", M. Kaneshige, Oct. 31, 2014.

Table 6. SITI Test Matrix. All tests include Swheat, unless noted. Additional details are listed below. WB-4* is the same as WB-4 except without Pb or Cr.

Salt		Liquid			
	None	DI H_2O	HNO_3+KS, pH 7	HNO_3+KS, Over[3]	HNO_3+KS, Under[4]
None		X (Control)	X[5]		
Na, Mg			X		
Na, Mg, Pb			X	X	X
LANL Pred.			X	X	X
LANL WB-4	X				
LANL WB-4*	X				
Eutectic[6]			X		
Eutectic, Pb			X		
Glove, TBD			X	X	X

Table 7. Parent drum composition predicted by LANL using Stream Analyzer software. Items in italics may be omitted.

Salt	Mass Fraction
$Al(NO_3)_3$*9H_2O	0.02378
$Ca(NO_3)_2$*4H_2O	0.09473
KNO_3	0.02076
*$Cr(NO_3)_3$*9H_2O*	*0.00125*
*$Fe(NO_3)_3$*9H_2O*	*0.06456*
H_2O-HNO_3-Al-Ca-Cr-Fe-Mg-Ni	*0.00194*
$Mg(NO_3)_2$*6H_2O	0.62319
HNO_3	0.01534
$NaNO_3$	0.13666
NaF	*0.00183*
*$Ni(NO_3)_2$*6H_2O*	*0.00061*
$Pb(NO_3)_2$	*0.00009*
$(COOH)_2$	*0.01527*

[3] Overneutralized acid will use 10% more KS than needed to achieve neutralization - a volume ratio of KS to 3.3M HNO_3 of 1.1:1.
[4] Underneutralized acid will use 10% less KS than needed to achieve neutralization – a volume ratio of KS to 3.3M HNO_3 of 0.9:1.
[5] Also, add KS to Swheat first, and then HNO_3. Does the order of mixing affect reactivity, as suggested by PNNL?
[6] The eutectic salt mixture is 67% $Ca_2(NO_3)_2$*4H_2O + 33% $Mg_2(NO_3)_2$*6H_2O.

Table 8. Parent drum compositions based on LANL WB-4 mixture. 0.2% water was omitted as negligible compared with waters of hydration.

Salt	Mass Fraction (w/25% Swheat)	Mass Fraction (not including Swheat)	Mass Fraction (not including Swheat, Pb, or Cr)
$Ca(NO_3)_2*4H_2O$	0.084	0.112	0.115
$Cr(NO_3)_3*9H_2O$	0.001	0.00134	
$Fe(NO_3)_3*9H_2O$	0.057	0.0762	0.0783
$Mg(NO_3)_2*6H_2O$	0.206	0.275	0.283
$NaNO_3$	0.367	0.491	0.504
$Pb(NO_3)_2$	0.019	0.0254	
$(COOH)_2$	0.014	0.0187	0.0192

Possible Variations:

1. Ramp and hold or other temperature profile. The planned tests will be continuous ramps, which has the advantage of taking the material through a range of temperatures in a reasonably short period of time, but a short test implies a fast ramp, which will not expose the material to lower temperatures for long. Instead, the temperature could be ramped to a fixed set point and held. For instance, biological activity might be accelerated by heating to modest temperatures (~40°C) without heating to higher temperatures where micro-organisms would be killed. Likewise, reactions occurring within a particular temperature range could be explored by slowing the ramp rate in that range while maintaining a fast ramp below (and above) to minimize test time.
2. Gas analysis. In vented configuration, some gas analysis (by RGA) or measurement of gas generation rate (by flowmeter) may be possible. These capabilities exist but are untested.